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PROCEEDINGS  
OF THE  
INDIAN ASSOCIATION  
FOR THE  
CULTIVATION OF SCIENCE  
VOL. I.

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PROCEEDINGS  
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Vol. I.

No. 1.

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Saturday, February 6th, 1915 at 4-45 P.M., Dr. P. C. Roy C.I.E., D.Sc., Ph.D., Vice-President, in the Chair.

*Tautomeric changes in Organic Thiobodies through the agency of mercuric nitrite, mercuric chloride, cupric chloride, platinic chloride and monochloro acetic acid.*

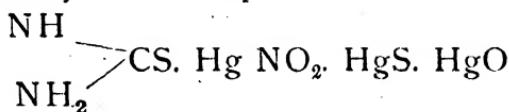
By Dr. P. C. Ray, C.I.E., D.Sc., Ph.D.

Rai Bahadur Dr. Chuni Lal Bose, I.S.O., M.B., F.C.S., was in the Chair when Dr. P. C. Ray read the above paper.

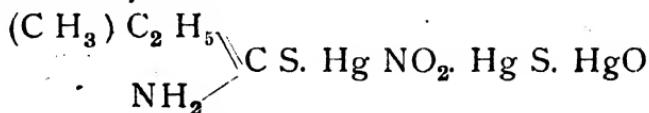
Through the agency of Mercuric Nitrite, ethyl mercaptan yields a nitromercaptide of the formula



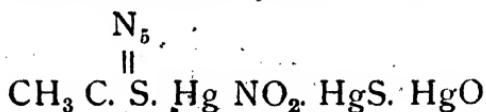
thiocarbamide yields a compound of the formula



alkylthiocarbamide yields

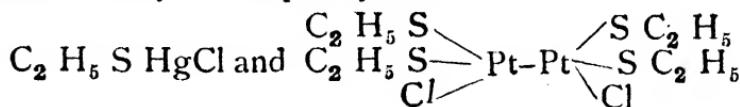


which is due to the presence of a potential mercapto group and thiocetamide yields

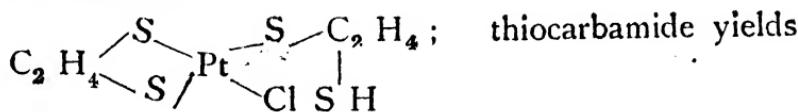


( 2 )

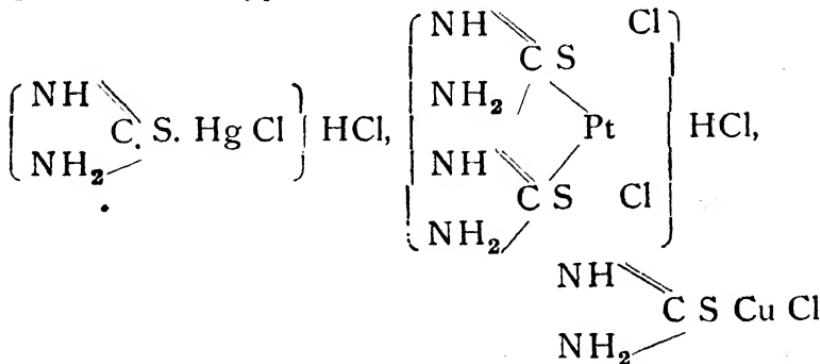
The same kind of changes have been found to take place through the agency of Cupric, Mercuric and Platinic Chlorides, with the formation of chloromer-captides. Ethyl mercaptan yields



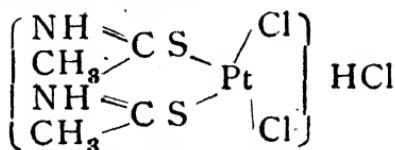
respectively with the corresponding chlorides. Thio-glycol yields with platinic chloride, a chloromeraptide of the formula



with mercuric, platinic, and cupric chlorides, compounds of the types

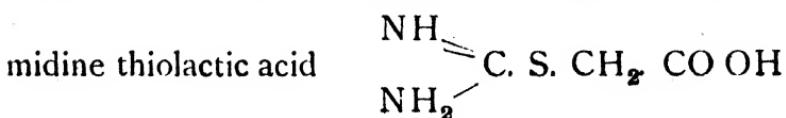


Thioacetamide gives with platinic chloride



Thiosemicarbazide and platinic chloride yield a compound of the formula  $\left[ \left( \begin{array}{c} \text{NH} \\ \diagdown \\ \text{C} \end{array} \right) \text{S} \right] \equiv \text{Pt Cl}_3 \text{ HCl}$

Thiocarbamide and monochloracetic acid form formal-



in aqueous solution though the hydrochloride of this is formed in acetone solution; mono-alkylthiocarbamide also yields corresponding substituted derivatives.

*A New Type of Salts : Mercuric Chloro-iodide.*

By Rasik Lal Datta, M.Sc.

Mercuric chloride has been prepared in two ways (1) by heating in a sealed tube mercurous chloride and iodine (2) by the careful sublimation of a mixture of mercuric chloride and mercuric iodide. Like mercuric iodide it turns yellow and that at a definite temperature. Its pyridine compound was also prepared. The constitution of the salt could not however be definitely assigned at present, on which further work is in progress.

*Experimental demonstration of Interference Fringes due to two point or linear sources nearly in line.*

By C. V. Raman, Esq., M.A.

In three papers published in the Philosophical Magazine for November 1906, January 1909 and May 1911, it has been shown by Mr. Raman that the diffraction-bands of the Fraunhofer class formed

by an obliquely-held rectangular aperture are unsymmetrical in character, both the width of the bands and the distribution of their intensity exhibiting this effect. Mr. Raman has since studied the case of two narrow rectilinear apertures parallel to each other in a plane on which the incident light fell very obliquely. The interference-fringes formed by the apertures at a great distance behind them or in the focal plane of the converging object-glass were exhibited at the meeting, and it was seen that they were also markedly unsymmetrical in character. The analogies and differences between this case and that of Newton's Diffusion-rings and the interference-rings of two point sources nearly in line were pointed out and explained. A full description with illustrative photograph, measurements and a mathematical discussion will appear in a special Bulletin.

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*On the Correlation of the Kamthi Beds.*

By Hem Chandra Das-Gupta, M.A., F.G.S.

Hitherto a two-fold classification of the Gondwana System has been generally accepted and these two groups are distinctly marked off from each other by very characteristic palaeobotanical considerations (1). In a small book on Indian geology by Mr. Vredenburg (2) the Gondwana System has been grouped into three main divisions—the lower, the middle and the upper. This three-fold division led me to study the question about the correlation of some of the Gondwana beds and the present note embodies the results I have arrived at.

The first attempt to establish a three-fold division of the Gondwanas was due to the late Dr. Feistmantel (3). His classification is given below and as my remarks apply only to the lower and the middle Gondwanas, the sub-division of the upper Gondwanas has been omitted.

Upper Gondwana.

Middle Gondwana      { Transitional beds.  
                                Panchet division.  
                                Damuda division.

Lower Gondwana      { Karharbari beds with fossils  
                                Talchir shales with fossils  
                                Talchir boulder bed without fossils.

Dr. Feistmantel correlated the lower Gondwanas with the Carboniferous-Permian and the middle with the Trias. This classification has also been practically

(1) A manual of the Geology of India, by R.D. Oldham p. 155.

(2) A Summary of the Geology of India, (second edition) p. 50

(3) Pal, Ind., Ser. XII, Vol. IV, p. XXV.

followed by Frech and Nætling (4) the only main difference being in the matter of correlation, as according to the authors of *Lethæa Geognostica* the lower Gondwanas correspond to the kohlenführende Dyas and also in the absence of any mention of the 'transitional beds'. Mr. Vredenburg's three-fold division, however, differs considerably from the groupings above referred to, as the following table will show:—

Upper Gondwana.	
Middle Gondwana	{ Maleri. Kamthi. Panchet.
Lower Gondwana	{ Damuda. { Raniganj. Ironstone shales. Barakar. Talchir. { Karharbari. Talchir.

So far as our present knowledge is concerned there cannot be any difference of opinion regarding the propriety of uniting the Talchir and the Damuda series of rocks under one main division—the lower Gondwanas, and my remarks will be confined towards the members united under the middle Gondwanas by Mr. Vredenburg with special reference to the correlation of the Panchet and the Kamthi series of rocks, because the relative position of the Panchet and the Kamthi beds, as shown above, appears to me to be of doubtful value.

For an account of the Panchet beds we are indebted to the late Dr. Meddlicott (5) and these beds contain, besides some vertebrate and invertebrate remains,

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(4) *Leth. Geogn. Pal.* Vol. II, pp. 608-609.

(5) *Mem. Geol. Surv. India*, Vol. III, pp. 126-137.

some plant fossils which will be mentioned in the sequel. Our first detailed knowledge about the Kamthi beds was derived from the observations of the late Dr. Blanford (6). Besides the occurrence in the Nagpur area, the Kamthi beds have also been met with chiefly in the Wardha valley coal-field (7) and in the Godaverry district (8). The well-known Kamthi flora will be enumerated later on.

We will now proceed to consider the chronological relation between the Kamthi and the Panchet beds. The Panchets are known to overlie the Raniganj beds but no section has as yet been recorded indicative of the relationship between the Panchet and the Kamthi series (9). In the Nagpur area the Kamthi beds have been found overlying the Talchirs while in the Wardha valley and in the Godaverry-Pranhita valley they have been found associated with the Barakars and in places the Kamthis have been found overlapping the Barakars (10) while evidences are also adduced pointing out to the possibility of a post-Barakar and pre-Kamthi denudation (11). This is all that is known about the relationship between

(6) Mem. G.S.I., Vol. IX, pp. 305 et. seq.

(7) Mem. G.S.I., Vol. XIII, pp. 66-81.

(8) Mem., G.S.I., Vol. XVI., pp. 208-211 and Mem. G.S.I., Vol. XVIII, pp. 250 et. seq.

(9) In his small treatise Mr. Vredenburg says "one observes sometimes a gradual passage from the Panchet to the Kamthi stage," (p. 58). I am, unfortunately, unable to follow this statement unless it is due to the fact that Mr. Vredenburg uses Kamthi and Pachmari as synonymous (p. 57).

(10) Mem. G.S.I., Vol. XIII, p. 67.

(11) Ibid. pp. 65-66.

the Damudas and the Kamthis in the field and from this we can only conclude that the Kamthi stage is younger than the Barakar stage, but no light is thrown about the mutual relationship between the Kamthi and the Panchet beds.

Stratigraphical evidence failing we have to apply to the organic contents. Mr. Vredenburg has correlated the Kamthi beds with the Rhaetic on the ground that *Danæopsis Hughesi* Feistm. has been met with in these beds (12). We are however unable to follow this statement for reasons given below.

According to the late Dr. Feistmantel (13) *Danæopsis Hughesi* is found in his Transitional beds, including under this epithet a group of peculiar beds with both lower and upper Gondwana fossils and found in the South Rewa Basin. Hughes found these beds to be more extensive than what was estimated by Dr. Feistmantel and these beds were styled as Supra-Barakars (14). It may be observed here that in course of a description of the Auranga coal-field flora, some beds have also been designated as Transitional Beds (15). These beds have no *Danæopsis Hughesi* and include chiefly the very common lower Gondwana fossils and on the scanty material available nobody can seriously think of correlating these two Transitional Series of rocks.

The inclusion of the Transitional beds with the Kamthi beds seems to be originally suggested by

(12) op. cit. p. 59.

(13) Pal. Ind., Ser. XII, Vol. IV, p. 6.

(14) Mem., G.S.I., Vol. XXI, p. 207.

(15) Pal. Ind., Ser. XII, Vol. IV, pt. 2, p. 11.

Hughes (16), though he himself was not very quite sure of it and thus the term Supra-Barakar, above referred to, was introduced instead of Transitional, but not Kamthi. This correlation appears to be doubtful and for this I shall, first of all, enumerate the plants that have been recorded from the Kamthi beds as well as from the Supra-Barakars.

## Kamthi fossils (17)

1. *Phyllotheia indica*
2. *Tueniopteris danoeides*
3. " *Feddeni*
4. " *cf. Mc. Clellandii*
5. *Glossopteris indica*
6. " *ampla*
7. " *Browniana*
8. " *angustifolia*
9. " *stricta*
10. *Gangamopteris cyclopterooides*
11. *Noeggerathiopsis hislopi*.
12. *Cardiocarpus* (?) *sp.*

## Supra-Barakar fossils (18)

1. *Schizoneura* (?)
2. *Asplenium whitbiense*
3. *Danœopsis Hughesi*
4. *Glossopteris indica*
5. " *ampla*
6. *Sphenopteris polymorpha*
7. *Thinnfeldia cf. odontopterooides*
8. *Noeggerathiopsis hislopi*

Comparison of these two lists brings out a few features which are remarkable. These features are:—

- (i) The presence of *Gangamopteris cyclopterooides* in the Kamthi beds and its absence from the Supra-Barakar.
- (ii) The presence of *Asplenium Whitbiense* and of *Thinnfeldia cf. odontopterooides* in the Supra-Barakar and the absence of these two genera from the Kamthi.

(16) Mem. G.S.I. Vol. XXI, p. 208.

(17) A manual of the Geology of India by R. D. Oldham p. 169; The Glossopteris flora by Arber., p. 206; Pal. Ind. New. Ser., Vol. II, Mem. I, p. 3.

(18) Pal. Ind. Ser. XII, Vol. IV.

(iii) The smaller number of species of *Glossopteris* in the Supra-Barakar beds than in the Kamthi and the absence of any new species in the former.

It is now known that *Gangamopteris* is confined to the Palaeozoic rocks (19), *Asplenium whitbiense* is Mesozoic (20) and *Thinnfeldia odontopteroides* is upper Triasic or Rhaetic (21). Thus the association of *Gangamopteris* with *Asplenium whitbiense* and with *Thinnfeldia odontopteroides* is not to be naturally expected and this is also corroborated by the evidence of the fossils cited above. About the third peculiarity attention will be drawn a little later on.

Though these two series of fossils differ from each other as stated above there are however three species which are common to both. These are *Glossopteris indica*, *Glossopteris ampla*, and *Noeggerathiopsis hislopi*. These three are, however, among the most cosmopolitan of the *Glossopteris* flora, the last being found even as far as Siberia (22).

The most important feature of the Supra-Barakars is, however, the presence of *Danæopsis Hughesi*. Besides being found in the Rewa basin, this species has also been met with in South Africa, China and Tonkin. In South Africa *Danæopsis Hughesi* has been obtained from the Burghersdorp beds or Upper Beaufort Series. These fossils have been described

(19) Seward : Fossil plant. Vol. II, p. 513.

(20) Ibid p. 344.

(21) Ibid p. 538.

(22) Mem. du Com. Geol. St. Petersburg. New Ser. Livr. 86 (1912).

by Prof. Seward (23) and, besides *D. Hughesi*, they include :—

1. *Schizoneura* sp.
2. *Taeniopterus carruthersi*.
3. *Glossopteris* sp.
4. *Odontopteris Browni*.
5. *Strobilites laxus*.
6. *Pterophyllum* sp. cf. *Tietzii*.
7. *Stigmatodendron dubium*.
8. *Thinnfeldia sphenopteroidea*.

In Tonkin *Danæopsis* cf. *Hughesi* Fstm. has been found in the island of Sommet Buisson. A rich flora has been found from this region. The fossils have been described by Zeiller (24) and the Rhætic age has been assigned to them.

The knowledge of *Danæopsis Hughesi*, as it occurs in China, is extremely meagre (25). This fossil has been found in the gorge near the village of San-schi-lipa ; no other fossil has been found associated with it while the beds underlying the *Danæopsis*-bearing beds have a *Glossopteris*-facies with *Cordaites*-like leaf which may be *Cordaites* or *Noeggerathiopsis hislopi*.

A comparison of the flora of the *Danæopsis-Hughesi*-bearing beds, as found in these areas, so wide remote, with the Kamthi fossils shows that the fossils found in these beds are all distinguishable

(23) Q. J. G. S. 1908. pp. 83-105; The Geology of Cape Colony by Rogers and Toit, p. 206.

(24) Etudes des Gites Min. France Paris, 1903.

(25) Denkschr. d. Kais. Akad. Wiss. Vol. LXX, 1901, pp. 144-

from the Kamthi fossils by (*a*) the absence of *Gangamopteris*, (*b*) the presence of many mesozoic genera and (*c*) a very limited occurrence of *Glossopteris*. From these considerations it becomes quite clear that the Kamthi beds are much older than the beds furnishing *D. Hughesi* (26).

The next point for discussion is the relative age of the Kamthi and the Panchet beds. For a solution of this question an appeal should be made to the floral evidence. The Kamthi flora has been given above and the following list includes the Panchet plants (27):—

1. *Schizoneura Gondwanensis.*
2. *Tæniopteris stenoneura.*
3. *Glossopteris indica.*
4. " *ampla.*
5. " *angustifolia.*
6. *Thinnfeldia cf. odontopteroides.*
7. *Cyclopteris (?) pachyrhaca.*
8. *Pecopteris concinna.*

(26). Very recently *Danaeopsis Hughesi* has been found by Zalessky from the upper Permian of the Petschora basin. The associates include *Gangamopteris rossica*, a species founded on leaves agreeing in shape and in the absence of a definite midrib with other forms of the genus, but distinguished by the rarity of anastomosis between the secondary veins, a feature regarded as due in part to imperfect preservation. The species may be identical with that described by Schmalhausen as *Zamiopteris glossopteroides*, which Zeiller compares with *Lesleya*. It is, however, interesting and suggestive that a few cross-connections occur between the veins, and it is by no means unlikely that Zalessky is correct in adopting the generic name *Gangamopteris*. The almost complete absence of anastomosis in some *Glossopteris*-fronds from India and South Africa affords a parallel case.

(Seward : Antarctic fossil plants 1914. p. 36).

(27) A manual of the Geology of India by R.D. Oldham p. 171 ; The *Glossopteris* flora by Arber.

A comparison of this with the Kamthi flora also brings out clearly the presence of some mesozoic plants, the absence of *Gangamopteris* and the smaller number of the species of *Glossopteris*. This last point requires a little elucidation.

A table is given below showing the distribution of the species of *Glossopteris* in the different Gondwana beds and it is quite clear that so far as the development of *Glossopteris* is concerned the genus begins from the Talchir, attains its maximum in the Raniganj and then begins to decline till it reaches the Jubbulpore stage where, according to Feistmantel (28), it is represented by a single species *Gl. cf. indica* and that no new species appeared after the Raniganj series.

(28). Pal. Ind. Ser. XI. Vol. II. p. 90.

Species.	Talchir.	Karhar-bari.	Bavakar.	Ironstone Shale.	Raniganj.	Kamthi.	Panchet.
1. <i>Glossopteris indica</i>	+	+	+	+	+	+	+
2. " <i>decipiens</i>		+	+				
3. " <i>ampla</i>		+	+	+	+	+	+
4. " <i>Browniana</i>			+			+	
5. " <i>intermedia</i>		+	+	..	+		
6. " <i>angustifolia</i>		+	+	+	+	+	+
7. " <i>retifera</i>		+	+	+	+		
8. " <i>conspicua</i>			+	+			
9. " <i>tortuosa</i>				+			
10. " <i>orbicularis</i>					+		
11. " <i>formosa</i>					+		
12. " <i>divergens</i>					+		
13. " <i>stricta</i>					+	+	
14. " <i>longicaulis</i>	+						

This list leads one to suspect that the Kamthi flora is older than the Panchet flora and this suspicion is further strengthened by a comparison of all the fossil plants found in the different series just referred to. The following table will exhibit this quite clearly :-

Species.	Talchir.	Karhar- bari.	Barukar.	Ironstone shale.	Raniganj.	Kamthi.	Panchet.
1. <i>Phyllotheeca indica</i>					+	+	
2. " <i>robusta</i>					+		
3. " <i>Griesbachii</i>		+	+				
4. <i>Schizoneura Wardii</i>	+		+				
5. " <i>gondwanensis</i>		+		+	+	..	+
6. <i>Actinopteris bengale- nsis</i>				+			
7. <i>Sphenophyllum speciosum</i>		+		..	+		
8. <i>Teniopterus danæ- oides</i>		+	+	+	+	+	
9. " <i>Roylei</i> (29)			+	+	+		
10. " <i>Feddeni</i>		+		+	+		
11. " <i>cf. McClellandii</i>				+	+		
12. " <i>cf. stenoneura</i>							+
13. <i>Dictyopteridium sporiferum</i>	+	..	..	+			
14. <i>Palaeovittaria Kurzi</i>				+			
15. <i>Glossopteris angustifolia</i>	+	+	+	+	+	+	+
16. " <i>indica</i>	+	+	+	+	+	+	+
17. " <i>ampla</i>	+	+	+	+	+	+	+

(29) In his *Glossopteris* flora Arber mentions two plants, *Cladophlebis Roylei* and *Cladophlebis sp.* as occurring in the Damuda beds (pp. 142-144). One of these, viz. *Cladophlebis sp.* is extremely fragmentary and no reliance can be put on it; the other was named *Pecopteris Lindleyana* by Royle and *Alethopteris Lindleyana* by Feistmantel while the arguments that have led Arber to refer this plant to *Cladophlebis* do not seem to be very conclusive. (Geol. Mag. 1901, pp. 548-549).

Species.	Talchir.	Karhar-bari.	Barakar.	Ironstone shale.	Raniganj.	Kamthi.	Panchet.
18. <i>Glossopteris decipiens</i>		+					
19. " <i>Browniana</i>			+	+	+	+	
20. " <i>intermedia</i>			+	+	..		
21. " <i>retifera</i>				+	+		
22. " <i>conspicua</i>				+	+		
23. " <i>divergens</i>				+	+		
24. " <i>stricta</i>				+	+	+	
25. " <i>formosa</i>				+	+	+	
26. " <i>orbicularis</i>				+	+	+	
27. " <i>tortuosa</i>				+	+	+	
28. " <i>longicaulis</i>				+	+	+	
29. <i>Gangamopteris cyclopterooides</i>	+	+	+	+	+	+	
30. " <i>angustifolia</i>	+		+			+	
31. " <i>Whittiana</i>					+		
32. " (?) <i>buriadica</i>		+					
33. <i>Neuropteridium validum</i>		+					
34. <i>Sphenopteris polymorpha</i>			+	..			
35. " <i>Hughesi</i>			+	+	+		
36. <i>Belemnopteris Wood-Masoniana</i>					+		
37. <i>Cyclopteris dichotoma</i>		+					
38. " <i>pachyrhacis</i>							+
39. <i>Pecopteris phegopterooides</i>					+		

Species.	Talchir.	Karhar- bari.	Barakar.	Ironstane shale.	Raniganj.	Kamthi.	Panchet.
40. <i>Peopteris concinna</i>							
41. <i>Merianopteris major</i>							
42. <i>Thinnfeldia cf. odontopteroidea</i>							
43. <i>Noeggerathiopsis Hislopi</i>	+	+	+	+	+	+	+
44. „ <i>Whittiana</i>							
45. „ <i>(?) lacerata</i>		..	..	..	+	+	
46. „ <i>(?) Stoliczkania</i>		+	+	..	+	+	
47. <i>Cardiocarpus indicus</i>		+	+	..	+	+	
48. „ <i>(?) Milleri</i>		+					
49. <i>Pterophyllum Balli</i>							
50. <i>Rhipidopsis ginkgooides</i>	+	+	+				
51. „ <i>densinervis</i>	+				+		
52. <i>Ottokaria bengalensis</i>	..						
53. <i>Voltzia heterophylla</i>				..	+	+	+

A comparison of this list leaves no room to doubt that the Kamthi flora is older than the Panchet flora but younger than the Raniganj flora as a whole.

The gradual passage of the Raniganj to the overlying Panchet may be used as an argument against accepting the Kamthi beds as being intermediate between the Raniganj and the Panchet. But a little consideration will show that this obstacle is not really so difficult as it appears to be.

While describing the Kamthi beds of the Wardha Valley coalfield, Hughes spoke of a Kamthi-Barakar unconformity due to a pre-Kamthi denudation (30). From this it is not unreasonable to think that while deposition in the Damuda basin was going on after the Barakars had been deposited, the conditions in the Wardha Valley and in the other areas where the Kamthi beds are developed were such as to render any fresh deposit impossible. In these areas the denuding agencies were in operation and this period of denudation practically coincided with the period of deposition of the whole of the ironstone shales and a great part of the Raniganj group and it is only when the uppermost members of this last group were being deposited that a migration of a part of the decaying Raniganj flora took place to the regions where the Kamthi beds are now found.

Mr. Vredenburg has put the Panchet, the Kamthi and the Maleri beds under the middle Gondwanas. We have given above our reasons for holding that the Kamthi beds are older than the Panchet. *Glosso-*

*Pteris* has been found all throughout these formations showing its period of initial stage, maximum development and practical extinction and it seems that this is an extremely important palaeontological point which should not be lost sight of in any scheme regarding the classification of the Gondwanas. Hence I think it advisable to follow the author of the Manual of Indian Geology and to unite all the *Glossopteris*-bearing beds under one group—the lower Gondwanas, the lower Gondwanas consisting chiefly of the following series of rocks :—

Panchet	Panchet
Raniganj (including the Kamthi beds towards the top)	}
Ironstone shale	Damuda
Barakar	}
Karharbari	}
Talchir	Talchir

It may be pointed out here that, while describing the Kamthi beds, the late Dr. Blanford was also led to formulate an opinion similar to that sketched above on the material then available (31) and this note of mine may be looked upon as an elucidation of the view suggested by the late illustrious deceased.

There now only remain the Maleri beds placed by Mr. Vredenburg at the top of his middle Gondwanas and considering the rich suite of vertebrate remains in these beds together with the complete absence of plant fossils, a distinction of these beds (and along with them of the beds at Tiki and at Denwa) into a separate group—the middle Gondwanas—might be desirable.

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(31) Mem., Geol. Surv. Ind. Vol. IX. pp. 329-330.



PROCEEDINGS  
OF THE  
**INDIAN ASSOCIATION FOR THE CULTIVATION OF SCIENCE.**

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Vol. I.

No. 2.

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Saturday, April 17th at 5 P.M., Dr. P. C. Ray,  
C.I.E., D.Sc., PH.D., F.C.S., Vice-President, in the Chair.

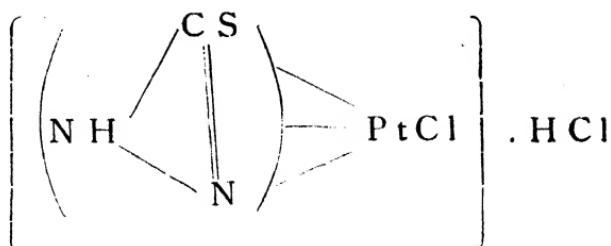
*Action of Monochloroacetic acid on  
Thiosemicarbazide.*

By FRANCIS V. FERNANDES.

(Preliminary Note)

It has been shown by Ray and Fernandes (Trans. Chem. Soc. 105, 2159) that thiocarbamide and simple monoalkylated thiocarbamides assume the tautomeric form in presence of monochloroacetic acid. The reaction takes place in the normal manner, the hydrogen of the thiol group of the thio-compound uniting with the chlorine of monochloroacetic acid; the hydrochloric acid thus formed is either fixed to the resulting base or eliminated according as whether the reaction takes place in acetone or aqueous solution, giving rise to the formation of formamidinethiolacetic acid, etc., or the hydrochlorides. Recently Ray has worked out a complete series of derivatives from platinic, mercuric, and cupric chlorides and numerous thio-compounds. The most remarkable of these derivatives is obtained from platinic chloride and thiosemicar-

bazide, which Ray holds to be thioldiazine of the following formula :—



It will be noticed here that the reaction is rather complicated, not only a molecule of hydrochloric acid but also a molecule of ammonia separating. This kind of splitting up of one or more molecules takes place when the reacting substances are very heavy, and consist of long chains.

It seemed desirable to study the reaction between monochloroacetic acid and thiosemicarbazide, as apart from the importance of thiosemicarbazide itself, a special interest centres in the tautomerism of the thio-compounds in general. Thus it appeared that some further light might be thrown on the mechanism of this kind of reactions.

#### EXPERIMENTAL.

Monochloroacetic acid and thiosemicarbazide were dissolved in water separately in molecular proportions, so as to form very concentrated solutions. When these two solutions were mixed together, a slight opalescence was observed, which however disappeared on standing for an hour or two. The mixture was kept overnight, when a beautiful crop of silky white crystals was formed. The product, although it appeared homogeneous and pure, was evidently a

mixture, as the analysis never gave any concordant results. The difficulty was increased by the fact that the substance possessed no melting point, but charred at about  $250^{\circ}$ . Moreover, it was found that the product was absolutely insoluble in all the ordinary solvents, *viz.*, alcohol, ether, benzene, acetone, ethyl acetate, acetic acid, etc. Thus it was impossible to purify the product by fractional crystallization.

The following method, when carried out carefully, gave invariably concordant results. The solutions of monochloro-acetic acid and thiosemicarbazide were made very concentrated, in fact, nearly saturated, and their mixture was allowed to stand just for 20-24 hours. The first crop of crystals that was then deposited was filtered, well washed with water, and dried in a vacuum desiccator. The mother-liquor gave a further crop of crystals, whose composition, however, was different from that of the first crop. The drawback in this method is that the yield of the pure product is very small, but it has the advantage of being the only way which is available at present to obtain the chemically pure substance.

#### ANALYSIS :—

0.1301 gave 0.1448 CO<sub>2</sub> and 0.0388 H<sub>2</sub>O.  
30.35 % C and 3.31 % H

0.0946 gave 0.1130 CO<sub>2</sub> and 0.0333 H<sub>2</sub>O.  
32.61 % C and 3.91 % H.

Mean is 31.48 % C and 3.61 % H.

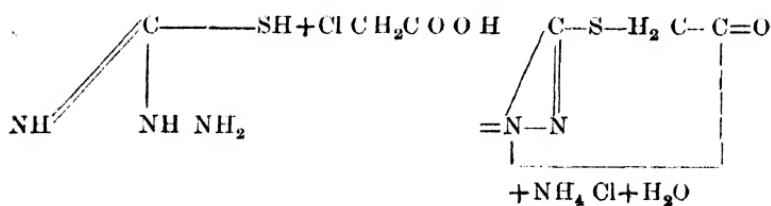
0.0530 gave 12.3 c.c. N<sub>2</sub> at  $29^{\circ}$  and 760 mm pressure 24.08 % N.

0.0419 gave 0.0873 BaSO<sub>4</sub> by fusion with Na<sub>2</sub>CO<sub>3</sub> and Na NO<sub>3</sub> 28.61 % S.

Duplicate analysis also confirmed the results in each particular.

#### CONSTITUTION.

The empirical molecular formula deduced from the results is  $C_8H_2N_2OS$ . Hence not only a molecule of hydrochloric acid separates in the reaction, but also a molecule each of ammonia and water. The reaction seems to proceed in the following direction —



This compound requires  $C = 31.57\%$ ,  $H = 1.75\%$ ,  
 $N = 24.56\%$  and  $S = 28.07\%$ .

Unless a peculiar molecular rearrangement takes place this formula is the simplest that can be deduced from the data. One chief reason to suppose that the reaction proceeds in the normal manner is that it occurs in the cold, and that no violent methods are employed to start or complete it.

It will be seen that the formula supports that given by Ray in the case of his thioldiazine.

The new compound is a remarkable one, as it consists of a ring within a ring. Only a few of such compounds are known.

Further work on the constitution is in progress.

In conclusion, I would like to offer my best thanks to Dr. Ray for giving every facility to carry on the above investigation.

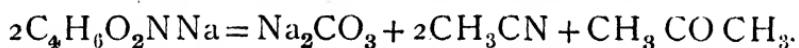
CHEMICAL LABORATORY,

*Presidency College, Calcutta.*

*Researches on Metallic Derivatives of Acid Amides.*  
*Part II. On the constitution of Metallic Derivatives of Acid Amides.*

By JITENDRA NATH RAKSHIT.

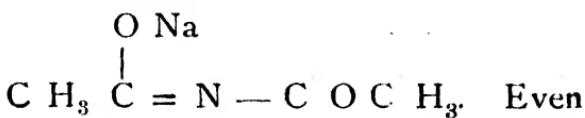
The metals in the metallic derivatives of ammonia must be assumed to have linked to the nitrogen, and similar would be the case with substituted ammonias; from which it is straight-forwardly imagined that they are similarly attached in those of acid amides. But both the acidic and basic properties expected to co-exist in the acid amides. Besides in a compound containing nitrogen and oxygen it is more probable that such electro-positive elements as sodium or potassium would prefer its connection to oxygen or in other words to the acidic portion to the basic portion of amidogen. The investigation was undertaken with a view to elucidate facts about their constitution. Titherly (Trans. Chem. Soc. 1897, 461; and 1901, 391) attempted to determine the position of the metals in such compounds but his conclusion is not very definite. For this purpose it was thought useful to observe the ultimate transformation of the metals when such compounds are allowed to decompose by heat. When sodium diacetamide was heated sodium carbonate was left as a residue and a mixture of methyl cyanide and acetone was distilled off.



As the residue was found to be pure sodium carbonate quite free from cyanide, hence the equation completely represents the reaction. It is remarkable to note that to perform the Lassaigne's test if the metallic sodium and acetamide were allowed to react at

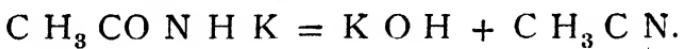
a higher temperature, sodium cyanide would certainly have been the product but, here, because they are only allowed to react through different stages, therefore such unusual results are formed. If the sodium were attached to the nitrogen, there would have been a greater chance of carrying with it to the last. The conclusion from the formation of the carbonate instead of cyanide of sodium is that the constitution of sodium

diacetamide is

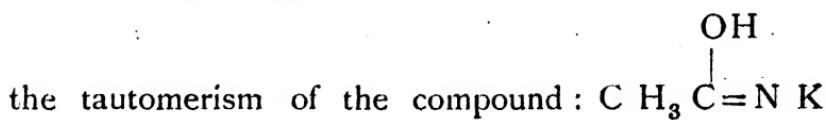


if it did not exist in this constitution originally it should have passed through this before splitting up into the above products.

When potassium cyanide is similarly heated caustic potash and methyl cyanide are formed.



But in this case the above equation does not strictly represent the whole reaction because always some potassium cyanide, ammonia and insoluble oil and a gas are invariably formed along with them. The attachment of  $-\text{C N}$  partly to the potassium and partly to the methyl radical can be reasonably ascribed to



or

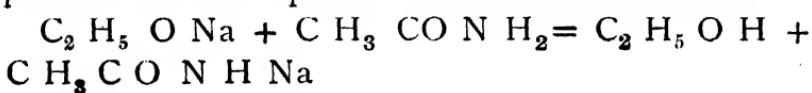


$\text{C H}_3 \text{ CO N H K}$  gives  $\text{KCN}$  and  $\text{C H}_3 \text{ C} = \text{N H}$  gives  $\text{C H}_3 \text{ C N}$ , the oxygen atom keeping its previous linkages to K or  $\text{C H}_3$  respectively. With these data however the tautomerism of the

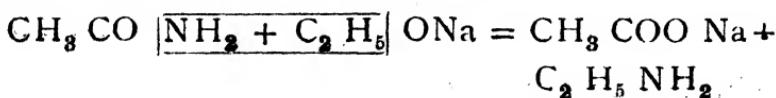
acetamides and their metallic derivatives cannot be conclusively established; only these and all the previous experimental observations can be better explained by its assumption.

*Reactions of alcohol with metallic derivatives of acid amides.*

Titherly (loc. cit. 467) has noted that sodium acetamide dissolves in alcohol without decomposition and subsequently explained its action on ethyl iodide in alcoholic solution (loc. cit. 392) with an assumption of its perfect stability there. If the sodium acetamide could remain stable in alcohol and does not decompose into sodium ethoxide and acetamide ( $\text{C}_2\text{H}_5\text{O}^- + \text{CH}_3\text{CO}^- \text{NH}_2 = \text{C}_2\text{H}_5\text{OH} + \text{CH}_3\text{CONH}_2$ ) then it is the simple conclusion that sodium acetamide is stabler than sodium ethoxide and if an alcoholic solution of the latter be mixed with acetamide it would produce or tend to produce some sodium acetamide.



Accordingly calculated quantities of 2 N solution of sodium ethoxide and acetamide were mixed to react according to the above equation and kept in a vacuum desiccator over sulphuric acid. Within half-an hour the inner side of the desiccator wherever some sulphuric acid was adhering was covered with white crystals. On opening the lid at that time a very strong odour like that of ammonia was perceived. Since water was absolutely excluded it was thought that the reaction may take place as :—



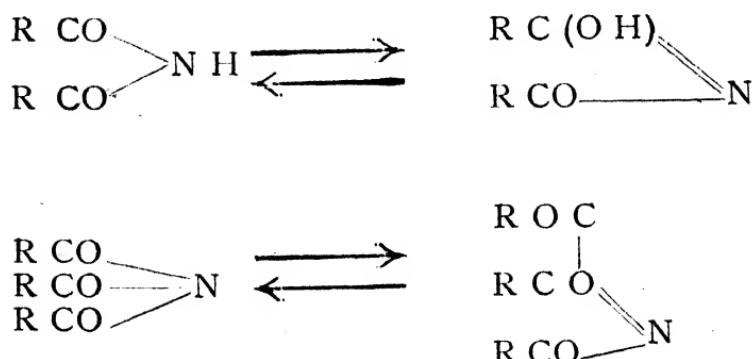
The residue was found to be pure and simple sodium acetate but the sulphuric acid was found to contain ammonia quite free from ethyl or any amine. Evidently to form ammonia under this circumstance one molecule of water is indispensable, and here it must have come from alcohol itself being transformed into ether (compare Scott Trans. Chem. Soc. 1909, 1200 ; Ray and Rakshit Trans. Chem. Soc. 1912, 217). Hence it is more probable that sodium acetamide, in alcoholic solution, decomposes into sodium ethoxide and acetamide. Again with the assumption of this hypothesis its reaction with methyl iodide can be more conveniently explained as it is known and always expected that sodium ethoxide would give methyl-ethyl-ether with methyl iodide.

The orange precipitate obtained by adding silver nitrate to sodium acetamide in alcoholic solution has been analysed and proved to be real derivative of acetamide but that which is temporarily left in solution and subsequently forms the white precipitate or the supposed other variety has not been quantitatively examined. So it is not yet known whether it is some additive compound or a real tautomer. Ostwald observed that acetamide being nonconductor has its constitution to be  $\text{CH}_3\text{CO NH}_2$  but this is not the general rule in the case of organic compounds such as alcohols, phenols etc. It is noted in this connection that in the cold the acid amides have the constitution as  $\text{R CO NH}_2$  and when heated they

$\text{OH}$   
pass to  
 $\text{R}-\underset{|}{\text{C}}=\text{NH}$

which is somewhat suggested from the experiments presently done. Subsequent

experiments will be undertaken to establish this statement, if possible. In the case of secondary and tertiary amides the constitutions are respectively as:—



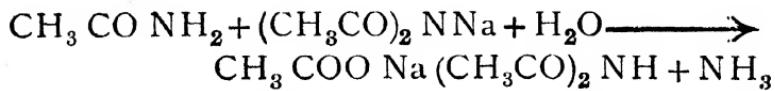
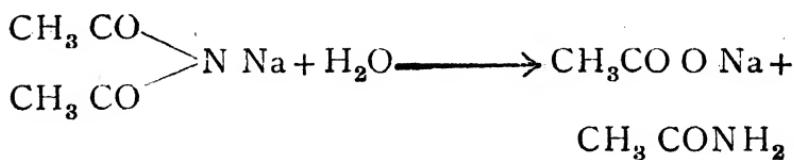
The whole assumption is based on a principle that when heated, basic character is changed to the acidic type producing the corresponding requisite rearrangement in the molecule.

When an alcoholic solution of sodium diacetamide (Trans. Chem. Soc. 1913) is added to an alcoholic solution of silver nitrate a brown precipitate is immediately formed which turns black in a few minutes. If the silver nitrate solution is added drop by drop to the other solution at the primary stage a pale orange precipitate is formed which disappears on shaking, being soluble in excess of sodium diacetamide. On adding more silver nitrate to it the brown precipitate becomes permanent and usually changes to black. Attempting to isolate the silver compounds similar difficulty was experienced as was in the case with the primary amide derivative. When 0.403 gm was dissolved in minimum quantity of absolute alcohol and kept in a vacuum desiccator over sulphuric acid

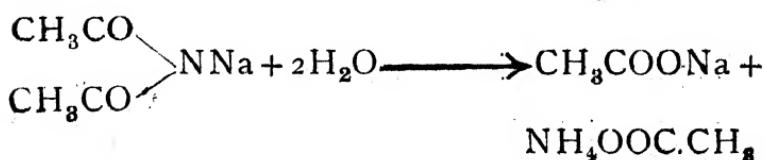
it dried in four days, without any loss or gain of weight.

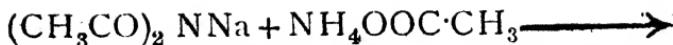
#### DECOMPOSITION WITH WATER.

In a platinum basin 0.760 gm of sodium diacetamide was dissolved in a minimum quantity of water. Immediately it did not give any perceptible odour of ammonia. It was kept in a vacuum desiccator over sulphuric acid. In about two hours the white crystals of ammonium sulphate became visible on the inner side of the desiccator, opening the lid a very strong odour of ammonia was noticed. The residue in the basin reached constant weight after three days and it was 0.819 gm. The increase in weight is 7.76 per cent. Adding strong sulphuric acid to the residue, odour of acetic acid was evolved. This hydrolytic decomposition must have taken place according to the following equations:—



or if the two molecules of water be allowed to react at once on one molecule of the compound then the equations, assuming the intermediate formation of ammonium acetate become:—





Both the equations, however, when summed up are represented by  $2 (\text{CH}_3\text{CO})_2\text{NNa} + 2 \text{H}_2\text{O} = 2 \text{NaOOC}\cdot\text{CH}_3 + (\text{CH}_3\text{CO})_2\text{NH} + \text{NH}_3$ ; and according to this hypothesis the increase of weight of the residue should be 7.72 per cent.

## DECOMPOSITION BY HEAT.

### I. *Sodium diacetamide.*

To study the decomposition by heat large quantities of the compound was prepared by the method described in Trans. Chem. Soc. 1913, 1559. It may be incidentally mentioned here that to avoid much contamination of the unacted-upon acetamide with crystals of the compound it is convenient to filter when ebullition has just ceased, the benzene remaining hot; instead of allowing it to cool as has been previously described. The unchanged acetamide remains as a heavy oily layer at the bottom and the crystals remain suspended in the benzene so that on decanting off the benzene on a filter paper practically all the crystals of the sodium derivative come along with it. The products of the different preparations were stored in a stoppered bottle after usual drying. Each time when the bottle was opened a distinct odour of ammonia could be immediately perceived. The substance being extremely hygroscopic rapidly absorbs moisture during transference which subsequently reacting according to the equation described above liberates ammonia.

Sixty-three grams of the substance were taken in a litre distilling flask and connected with a condenser. Gently heating, it began to melt at the contact of the sides of the flask and to decompose giving off a vapour which condensed as a colourless liquid. Practically the whole liquid was collected within 80°C. As the rate of the collection of the liquid was gradually diminished it was more and more strongly heated. From 80°C, the temperature almost suddenly rose to 210°C and then slowly to 215°C, but very little was distilled or collected. During the process of decomposition the substance first melted then gradually gave off the vapour which condensed to the above mentioned liquid and the residue was by and by solidified being finally transformed into sodium carbonate. Thus layer after layer it was completely decomposed and a solid, slightly blackish residue was left in the flask. When cooled it was dissolved in water and filtered. The insoluble residue was carefully washed and dried. It was found to be 0·2 gm carbon. The filtrate was sodium carbonate pure and simple absolutely free from any cyanide. Sometimes at the last part, especially when the substances are old, small amounts of brown liquids distil over at 210—218°C and solidifies at the neck of the condenser. These have been found to be primary or secondary acetamide or their mixture. In one case when it was dried in vacuum over sulphuric acid it melted at 80°5 C and gave H = 8·6 and C = 42·1 per cents and acetamide requires H = 8·4 and C = 40·7. In another case it gave 20·07 per cent nitrogen whereas primary and secondary acetamides require 23·28 and 13·59 per cents respectively ; so it was a mixture.

The crude distillate of the above experiment was 17.8 gms. It was kept over night with anhydrous potassium carbonate and then distilled for fractionation ; when heated on water bath 10.5 gms were collected at 68-80°C, within a few minutes. After this the thermometer constantly indicated 84°C for about half an hour but no liquid came out. On removing the water bath when heated on an asbestos wire guage the temperature uninterruptedly rose to 215°C and a small quantity of the liquid was distilled which very soon solidified to a transparent crystalline mass. It was recrystallised from benzene and found to give 18.03 per cent nitrogen and was subsequently confirmed to be a mixture of acetamides

The liquid collected at 68-80°C was redistilled on waterbath and two fractions were collected ; the first at 70°-72°C and the second at 73°-80°C.

#### *Examination of the first fraction.*

- I 0.2186 gm gave 0.4856 gm CO<sub>2</sub>; 0.1650 gm H<sub>2</sub>O; C=59.90 and H=8.40.
- II 0.1340 gm gave 0.2965 gm CO<sub>2</sub>; 0.1068 gm H<sub>2</sub>O; C=59.90 and H=8.86.
- III 0.2100 gm gave 33.5 c.c. N<sub>2</sub> at 22°C and 760 mm N=17.96.
- IV 0.1554 gm gave 24.6 c.c. N<sub>2</sub> at 31°C and 760 mm N=17.04.

It gave Gunning's reaction for acetone by dissolving mercuric oxide and also iodoform in the cold with iodine and caustic soda or ammonia. Two drops of the liquid were taken in a test tube and diluted with

5 c.c. absolute alcohol, then a piece of freshly cut clean sodium was put into it. After the sodium was dissolved it developed the characteristic odour of ethylamine (cf. Rakshit Jour. Amer. Chem. Soc. 1913, 445), and it gave carbylamine when heated with chloroform. Thus it gives all the confirmatory tests for both acetone and acetonitrile. In estimating acetone by Messenger's method 0.1285 gm required 62.7 c.c.  $\frac{N}{10}$  iodine, whence the percentage of acetone in the sample is 47.19.

Now if remainder 52.81 per cent be methylcyanide then percentages of carbon, hydrogen and nitrogen in the mixture become 59.83, 8.70 and 17.81 respectively. These fairly agree with the results obtained by actual analyses.

#### *Second fraction.*

- I. 0.1666 gm gave 0.3605 CO<sub>2</sub>, 0.1158 H<sub>2</sub>O C = 59.02, H = 7.72.
- II. 0.1170 gm gave 31.4 c.c. N<sub>2</sub> at 32°C and 760 mm pressure, N = 28.67.
- III. 0.1442 gm gave 38.0 c.c. N<sub>2</sub> at 32°C and 760 mm pressure, N = 28.16.

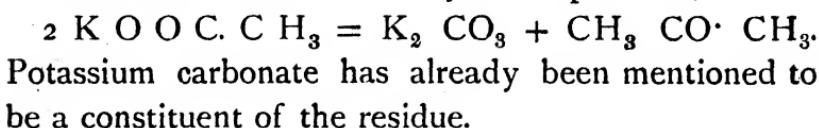
This substance also gave qualitative tests for acetone and methyl cyanide as the other fraction. In estimating acetone by Messenger's method, 0.2464 gm required 41.6 c.c.  $\frac{N}{10}$  iodine which is equivalent to 16.34 per cent acetone. Assuming the rest 83.66 per cent to be methyl cyanide percentages of carbon, hydrogen, and nitrogen become 59.01; 7.80 and 28.51 respectively. These also agree with the above results.

## POTASSIUM ACETAMIDE.

Seventy-two grams of potassium acetamide (loc. cit.) was similarly heated as sodium diacetamide. This also melted and solidified by parts after decomposition giving a colourless liquid and a gas. The gas, having an odour of ammonia was passed through dilute hydrochloric acid ; but there was some small quantity of gas which was continually found to escape absorption in the acid. The hydrochloric acid solution was evaporated and was found to contain only ammonium chloride free from any amine.

The residue in the flask was caustic potash largely contaminated with potassium cyanide and a small quantity of carbonate. In this case also there was slight charring but its quantity was much smaller. The total liquid collected was 10.0 c.c. and weighed 9.0 gm. It was left over night with anhydrous potassium carbonate and then distilled for fractionation on water-bath. The first portion was collected at 72-73°C, and the rest up to 82°C. The first fraction on reduction with alcoholic sodium gave ethylamine, which on heating with chloroform gave very strong odour of carbylamine. It is wholly soluble in water. It gives iodoform and Gunning's reaction for acetone. When estimated by Messenger's method 10.11 per cent acetone was found 0.0880 gm requiring 9.2 c.c.  $\frac{N}{10}$  iodine. So the product is methyl cyanide mixed with acetone. The formation of acetone during the process of decomposition may be reasonably ascribed to the decomposition of potassium acetate formed by the hydrolysis of the compound, by the unavoidable

absorption of moisture from air owing to its extreme hygroscopic nature. The reaction takes place as,  
 $\text{CH}_3\text{CO NHK} + \text{H}_2\text{O} = \text{CH}_3\text{COOK} + \text{NH}_3$ , which is suggested from the fact that whenever the bottle of substance is opened, which was previously left loosely stoppered for sometime a very strong odour of ammonia is perceived. And the potassium acetate thus formed eventually decomposes as,



The second fraction was similar in appearance and odour as the first one, but it does not, however, completely dissolve in water but a very small quantity of an oily drop is left floating at the top. It gave amine and then carbylamine just as others did. It gave all qualitative tests for the presence of acetone. 0.067 gm required 3.2 c.c.  $\frac{N}{10}$  iodine for converting into iodoform hence the percentage of acetone is 4.62, the yield of the oily product being small and also the oil itself being sensibly soluble in water its systematic examination was not successfully done.

In conclusion I wish to express my thanks to the Research Fund committee of the Chemical Society of London for a grant for the "continuation of the researches on metallic derivatives of acidamides," which has partly defrayed the cost of the investigation.

Presidency College,  
*Calcutta.*

PROCEEDINGS  
OF THE  
**INDIAN ASSOCIATION FOR THE CULTIVATION OF SCIENCE,**

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Vol. I.

No. 3.

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Saturday, September 18th, 1915, at 5 P.M., Dr. P. C. Ray, C.I.E., D.Sc., Ph.D., Vice-President, in the Chair.

*On the Relationship of the Atomic Volumes and the Specific gravities of the elements.*

By MANINDRA NATH BANERJEE, F.C.S.

PRELIMINARY NOTE.

The *atomic volumes* and the *specific gravities* of the elements are correlated and the ratio  $\frac{\text{at. vol.}}{\text{sp. gravity}}$  (of the elements) or simply  $\frac{A}{D^2}$  (where A represents the atomic weight and D the density or the specific gravity of the element either in the solid or the liquid state,  $\frac{A}{D^2}$  being the atomic volume) is a physical property of the element indicating its degree of condensation at a particular temperature, and as such it has a definite relation with the *chemical energy* or better the force of *chemical affinity* of the element or more simply,

*Force of Chemical affinity (of an element) = f degree of condensation of an element, at any particular temperature, as indicated by its physical property  $\frac{A}{D^2}$  (where A stands for the atomic weight and D, the*

*specific gravity* of the element either in the solid or liquid state,  $\frac{A}{D}$  being the atomic volume of the element), that is,

$$\text{FORCE OF CHEMICAL AFFINITY} = f \frac{A}{D^2}$$

It has long been observed by renowned chemists (Mendeleeff, Loether Meyer) that the atomic volume rises and the specific gravity falls with the lighter elements while it is reverse in the case of the heavier elements. But the lighter elements, such as F, Cl etc., on the one hand and Li, Na, K, etc., on the other are chemically very energetic, hence it may be said, that the chemically active elements have high atomic volumes and low densities. The importance of this relationship may be illustrated by curves of the atomic volumes of the elements referred to the specific gravities, as well as of the ratio  $\frac{\text{at. vol.}}{\text{sp. gr.}}$  referred to the atomic weights. In the former (which has been studied in three different ways), the positions occupied by the elements being joined to the origin form angles with the horizontal axis represented by  $\theta$ , which most significantly brings out a relationship *viz.*,  $\frac{\text{at. vol.}}{\text{Density or sp. gr.}}$  (of the elements)  $= f\theta = \tan \theta$ , while the latter curve has some special characteristics which mark it out from that of the atomic volumes of Loether Meyer. So the importance of the relationship of atomic volumes and the specific gravities of the elements being indicated, its physical significance may be drawn from certain experimental and theoretical data. The bare experimental facts, that at very low temperatures no chemical reaction whatever can take place, while at very high temperatures no chemical reaction also is quite possible, prove that

the *reaction velocity* which is a function of absolute temperature determines chemical reaction between certain limits only, that is, with high and low reaction velocities, as at very high and low temperatures, there being no chemical action at all, it may be conclusively drawn that chemical action only takes place between certain limits of the reaction velocity, i.e., between some maximum and minimum points of it. Again since the *mean kinetic energy of translatory motion* of any particle is a function of the absolute temperature, it is certainly related to the volume of it being also a function of the absolute temperature ; or, in other words, if the volume of a substance increases (with the rise of temperature), the kinetic energy of translatory motion of its molecules increases or the *vis-viva* becomes greater and on the other hand, if the volume diminishes, that is to say, the density increases, the *vis-viva* decreases too. But the reaction velocity in any substance being a function of the absolute temperature, it is in relationship with the mean kinetic energy of translatory motion of its molecules. Evidently, therefore, the mean kinetic energy of translatory motion or the *vis-viva* in the molecules of a substance determines its reaction velocity at any particular temperature. But the mean kinetic energy of translatory motion of the molecules of any substance at any temperature being, as mentioned before, proportional to the volume it occupies at that particular temperature, and, therefore, inversely proportional to its density at that temperature, its reaction velocity becomes proportional directly to the volume it occupies at that temperature and inversely to its density

at that temperature. Again since the reaction velocity of any substance at any particular temperature determines its chemical activity at that temperature, its volume and density or in other words, the state of its condensation at that particular temperature as well determines its chemical activity. For with increasing *reaction velocity* the reacting substances occupy larger *volumes* and have correspondingly smaller *densities* hence they become more porous (as Mendeleeff has observed) and therefore less condensed. Thus the particles within move quite freely, and the velocity being greater the collision or impact between heterogeneous molecules becoming violent too, effect chemical union easily. Evidently the degree of condensation of matter, as Mendeleeff observes, influences the course of chemical transformation. Thus we have the relationship of *chemical activity* of a substance at any temperature expressed in relation to that of its *volume* and *density* at that particular temperature, or in other words the chemical activity of a substance becomes a function of the ratio  $\frac{\text{Volume}}{\text{Density}}$ . But as the chemical activity of a substance is a function of its reaction velocity and between certain limits of it, (as we have pointed out before), so it is also a function of  $\frac{\text{Volume}}{\text{Density}}$  and between certain limits of it too, *i.e.*, either with very high values of  $\frac{\text{Volume}}{\text{Density}}$  (corresponding to rise of temperature or to some physical conditions even at the ordinary temperature) or with very low values of  $\frac{\text{Volume}}{\text{Density}}$  (corresponding to a fall of temperature or to some physical conditions even at the ordinary temperature) the chemical activity becomes very low. But as we cannot know the absolute volume and absolute density

of a substance at any temperature, we must have to fall upon specific relations and hence a connection of the chemical activity with that of the relationship  $\frac{\text{at. vol.}}{\text{sp. gr.}}$  may be indicated, or in other words we may say—  
 FORCE OF CHEMICAL AFFINITY =  $f \frac{A}{D^2}$  (and this too is a maximum-minimum function.)

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### *A New ammonio-copper ferrocyanide compound.*

By DR. SARASI LAL SARKAR, M.A.

#### Preparation of the Compound.

A new ammonio-copper ferrocyanide compound has been prepared by the writer in the following way.

Potassium ferricyanide solution and copper sulphate solution each of moderate strength are mixed together, when a turbid solution, containing the yellowish brown precipitate of cupriferricyanide is produced. A sufficient quantity of ammonia is added to this mixture till the precipitate is dissolved. A grass-green coloured solution is thereby produced. This solution being left standing for a few days, precipitates gradually a reddish brown coloured substance which reveals a crystalline structure of rectangular prisms either on microscopical examination or sometimes to the naked eye appearance.

This crystalline precipitate can also be obtained from an ammoniacal solution of chemically pure ferricyanide, which is also a grass-green coloured solution like the one previously described. I have noticed the fact that the formation of this yellowish brown crystalline precipitate becomes much copious and rapid

whenever there is excess of potassium ferricyanide in the solution, otherwise the precipitation is exceedingly slow.

Qualitative examination reveals the presence of Cu, Fe, NH<sub>3</sub> and hydro-ferro-cyanic acid. The presence of K sulphuric acid and hydro-ferri-cyanic acid are specially looked for but are found to be absent. Copper is found to be present in cupric state.

It may be noted that though potassium ferricyanide solution has been used for preparation of the substance, the substance is a ferrocyanide compound and not a ferricyanide.

It is found that by washing the substance with distilled water, minute traces of ammonia passes off with the filtrate. Quantitative analysis of the substance has been carried on with different samples. So the samples have been prepared by washing the precipitate with dilute ammonia instead of distilled water. The precipitate after being washed is kept up in a dessicator till this attains a constant weight and then it is taken up for analysis.

#### Estimation of Copper.

##### *Experiment I :—*

0·575 grms. of the substance taken, which is decomposed by heating with strong sulphuric acid, the residue dissolved in dilute hydrochloric acid and copper precipitated by H<sub>2</sub>S as sulphide, which being filtered off and washed, again dissolved in HCl and H<sub>2</sub>S being driven off by heat copper is precipitated by caustic potash solution and is estimated as oxide. From 0·575 grms of the substance the amount of

copper oxide obtained is 0.1913. From this it can be calculated that the percentage of copper present in the substance is 30.06.

*Experiment II :—*

0.200 grms substance taken, which is decomposed with sulphuric acid and residue dissolved in dilute hydrochloric acid as before, from which copper is precipitated with sodium thiosulphate and estimated as sulphide. The amount of copper sulphide found in 0.2000 grms. of the substance is 0.0776 grms. from which copper present is 31.00 per cent.

*Experiment III :—*

In this experiment done exactly in the above way, the substance taken is 0.2016 grms. CuS obtained is 0.0784 grms. Hence Cu present is 31.04 per cent.

Estimation of Iron.

*Experiment No. I :—*

0.514 grms. substance taken, decomposed by ignition and the residue dissolved in HCl, Cu is eliminated by  $H_2S$  as sulphide and from the filtrate, iron is precipitated as hydrate and estimated as oxide in accordance with the usual method, which is actually found in this case to be 0.1015 grms whence iron is 13.80 per cent present.

*Experiment II :—*

In this experiment done exactly in the above way from 0.4046 grms. of the substance, 0.0786 grms. of  $Fe_2O_3$  is obtained from which Fe present is 13.58 per cent.

*Experiment III :—*

0·4698 grms. of the substance taken which is decomposed with strong  $H_2SO_4$  and the residue dissolved in dilute HCl and made up to 200 cc. The solution is divided into two equal parts from each of which iron is precipitated as hydrate and estimated as oxide.

The amount of  $Fe_2O_3$  obtained from the 1st solution is 0·0495 grms. from which Fe present is 14·78 per cent.

The amount of  $Fe_2O_3$  obtained from the 2nd solution is 0·0483 grms. from which Fe present is 14·38 per cent.

The average of the two experiments is 14·58 per cent.

Estimation of ammonia.

*Experiment I :—*

0·3716 grms. of the substance taken, which is distilled with caustic potash and the distillate collected into 10cc of  $\frac{N}{2} H_2SO_4$  diluted with distilled water. When the distillation is finished, the amount of  $H_2SO_4$  which has not been neutralized is estimated by titration with  $\frac{N}{6}$  caustic soda. The amount of caustic soda solution required for the purpose in this experiment is 5·80 cc. Hence ammonia present in the substance is 17·56 per cent.

*Experiment II :—*

0·8138 grms. of the substance taken of which the distillate is collected as before into 20 cc. of  $\frac{N}{2} H_2SO_4$  and the amount of  $\frac{N}{6}$  caustic soda solution required for the unneutralized acid is 12·8 cc. From this ammonia present in the substance is 15·53 per cent.

*Experiment III :—*

0·8760 grms. of the substance taken which is distilled as before into 20 cc. of  $\frac{N}{2}$  H<sub>2</sub>SO<sub>4</sub> and the unneutralized acid required 8·4 cc. of  $\frac{N}{5}$  NaOH which gives 15·00 per cent. of ammonia to be present in the substance.

Estimation of total Nitrogen.

*Experiment I :—*

0·0988 grms. of the substance taken, from which the total nitrogen is set free by Kjeldal's method and is collected into 10 cc. of  $\frac{N}{2}$  H<sub>2</sub>SO<sub>4</sub>. The amount of unneutralized acid present is determined by titration with  $\frac{N}{5}$  KOH of which 12·7 cc. is required in the present case. Hence total Nitrogen present is 34·85 per cent.

*Experiment II :—*

Another experiment similarly done by taking 0·100 grms. of the substance and collecting the resultant ammonia into 10 cc. of  $\frac{N}{2}$  H<sub>2</sub>SO<sub>4</sub>. The amount of  $\frac{N}{5}$  KOH required for the neutralization of the unneutralized acid in this case is 12·50 cc. from which the amount of total nitrogen present is 35·00 per cent.

*Experiment III :—*

The percentage of nitrogen is determined by Dumas method and is found to be 35·20 per cent.

Combustion analysis.

*Experiment I :—*

0·1598 grms. of substance taken, weight of which after combustion is 0·0934 grms., i.e., the residue is 58·44 per cent of the original substance.

$$\begin{array}{rcl} \text{Wt. of caustic potash tube + CO}_2 & = & 56.3206 \\ \text{Weight of KOH tube} & = & 56.2212 \\ \hline \end{array}$$

$$\begin{array}{rcl} \text{CO}_2 \text{ present} & = & 0.0994 \\ \text{which gives } 16.96 \text{ per cent carbon present.} & & \end{array}$$

$$\begin{array}{rcl} \text{wt. of CaCl}_2 \text{ tube + H}_2\text{O} & = & 50.5002 \\ \text{wt. of CaCl}_2 \text{ tube} & = & 50.4472 \\ \hline \end{array}$$

$$\begin{array}{rcl} \text{H}_2\text{O present} & = & 0.0530 \\ \text{which gives } 3.68 \text{ per cent H}_2 \text{ present.} & & \end{array}$$

*Experiment II :—*

0.1004 grm. substance taken, weight of which after combustion is 0.0592 grms. which is 58.96 per cent.

$$\begin{array}{rcl} \text{wt. of KOH tube + CO}_2 & = & 56.2212 \\ \text{wt. of KOH tube} & = & 56.1560 \\ \hline \end{array}$$

$$\begin{array}{rcl} \text{CO}_2 \text{ present} & = & 0.0652 \\ \text{which gives } 17.50 \text{ per cent carbon.} & & \end{array}$$

$$\begin{array}{rcl} \text{wt. of CaCl}_2 \text{ tube + H}_2\text{O} & = & 56.4244 \\ \text{wt. of CaCl}_2 \text{ tube} & = & 56.3898 \\ \hline \end{array}$$

$$\begin{array}{rcl} \text{H}_2\text{O present} & = & 0.0346 \\ \text{which gives } 3.82 \text{ per cent of H}_2. & & \end{array}$$

Percentage of residue after ignition.

In connexion with combustion analysis just described, I have noted that the percentage of residue after combustion in two experiments to be respectively 58.44 per cent and 58.96 per cent.

Similar result can be obtained by igniting the substance over a blow-pipe. For example I took 1.5326 grms. of the substance which after ignition gave 0.895 grm. of residue which gives 58.40 per cent.

The result of another similar experiment is 58.22 per cent.

## Theoretical formula of the substance.

It will be seen from the following table that the results obtained from the analysis correspond with the theoretical percentages as calculated from the formula  $\text{Cu}_2 \text{FeC}_6\text{N}_6 \cdot 4 \text{NH}_3$ . Now a substance having the above formula if strongly ignited will leave a residue consisting of  $\text{CuO}$  and  $\text{Fe}_2\text{O}_3$ . If we start with two molecules of the substance, viz.,  $2\text{Cu}_2 \text{FeC}_6\text{N}_6 \cdot 4 \text{NH}_3$  the residue after ignition will be  $4 \text{CuO} + \text{Fe}_2\text{O}_3$ . Molecular weight of two molecules of substance is 814.2.

Molecular weight of  $4 \text{CuO} + \text{Fe}_2\text{O}_3$  is 478.2.

$$\therefore \frac{\text{wt. of residue after ignition} \times 100}{\text{wt. of substance taken}} = \frac{478.2 \times 100}{814.2}$$

$$= 58.73 \text{ per cent.}$$

It will be seen from the annexed table that this theoretical percentage of residue also corresponds closely with the result actually obtained.

	Experiment I.	Experiment II.	Experiment III.	Average of previous experiments.	Calculated from theoretical formula.
Percentage of Cu ...	30.06	31.00	31.04	30.70	31.24
do. of Fe ...	13.80	13.58	14.58	13.98	13.73
do. of $\text{NH}_3$ ...	17.08	15.53	15.00	15.87	16.70
do. of total N ...	34.85	35.00	35.20	35.01	34.39
do. of C ...	16.96	17.50	...	17.23	17.68
do. of $\text{H}_2$ ...	3.68	3.82	...	3.75	2.94
Percentage of residue after ignition.	58.44	58.96	58.40	58.60	58.73

A newly discovered compound or not ?

Searching carefully through the literature, it appears that none has noticed previously to me that an ammoniacal solution of copper ferricyanide when kept for sometime gives a crystalline precipitate of a definite chemical compound. However some of the previous workers have described compounds, having analogous composition, which requires comparison with the one obtained by me.

The following occurs in Gmellin's book on Chemistry Vol. VIII.

" $4 \text{ NH}_3, \text{C}_6\text{N}_3 \text{Fe Cu}_2$  (Cyano ferrure de cuvre biammoniacal). Ferrocyanide of copper digested with aqueous ammonia diminish in bulk and becomes green and crystalline, but if the ammonia be poured off and water added the combined ammonia dissolves out and the red colour is restored. This experiment may be repeated *ad libitum*; the decanted ammonia is pale green containing but a small quantity of copper in solution and when mixed with water in closed glass vessels, deposits an orange yellow substance (Vauquelin Ann Chem Phys, 9, 120, also schow 25,60)."'

It will be easily seen that the substance described above possesses physical characteristics entirely different from those of the substance prepared by me and hence is a distinct substance. The above also holds true regarding another substance described by Gmellin to which he ascribes the formula " $4 \text{ NH}_3, \text{C}_6\text{N}_3 \text{Fe Cu}_2 + \text{Ag}$ ".

J. Messner, a German chemist carried on a research regarding ferrocyanide compounds and his researches have been published in Ziet Anorg Chemie 8, 363—393. A summary of the article has been published in

the Journal of the Chemical Society Abstracts 1895, part I, pages 405 to 407.

The following is an extract from the above summary. " $\text{Cu}_2(\text{Fe C}_6\text{N}_6)$ , 8  $\text{NH}_3$  is obtained by adding a solution of ammonium ferrocyanide in strong ammonia to a solution of cuprous chloride in the strongest ammonia and allowing the mixture to remain for a few hours. It crystallizes in beautiful black, lustrous prisms, is very soluble in ammonia and is not decomposed by cold absolute alcohol. The crystals on exposure to air quickly decompose into ammonia, copper ferrocyanide and the compound,  $(\text{Cu}_2 \text{Fe C}_6\text{N}_6)$ , 4  $\text{NH}_3$ ."

It will be seen from the above description that the substance obtained by J. Messner which occurs as a decomposed product, must be an amorphous substance, hence a different substance from that obtained by the writer which is a crystalline substance, though both these substances possess identical chemical formula *viz.*,  $\text{Cu}_2 \text{Fe C}_6\text{N}_6$ , 4  $\text{NH}_3$ .

Above I have tried to give all the references I have been able to find out from the literature about the substances possessing analogous Chemical formula with that obtained by me and as I have shown that all these substances obtained by other workers possess different physical characteristics from those of substance obtained by me, I may conclude that the substance described in this paper is a chemical compound which has not been previously obtained by other chemists.

In conclusion I beg to thank the authorities of the Indian Association for the Cultivation of Science for their kindly allowing me to work in the laboratory of the Association.

*Experimental Demonstration of Combinational Vibrations.*

By C. V. RAMAN M.A.

In Bulletin No. 11 of this Association and the Physical Review for January 1915, the author has shown how two tuning-forks simultaneously varying the tension of a string stretched between them, may maintain vibrations whose frequencies are related jointly to those of the two forks. By using electrically maintained forks, the vibrations of the string thus maintained may be readily projected on the screen. This was shown at the meeting, and the various frequencies of vibration and their corresponding forms became very evident to the audience.

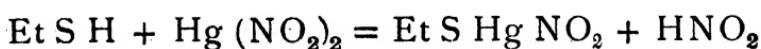
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The Chairman vacated the Chair and Dr. B. L. Chaudhury occupied it.

*Synthesis of the Salts of the Sulphonium Series  
with two Sulphur Atoms.*

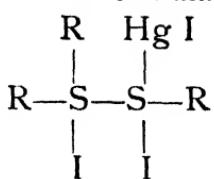
By Dr. RAY, C.I.E., D.Sc., Ph.D.

It is found that when mercuric nitrite acts upon the mercaptans (*e. g.*, methyl and ethyl mercaptans) a class of crystalline bodies are obtained. Thus :



These nitromercaptides, when treated with an alkyl iodide, give rise to a series of compounds of the Disulphonium type, having the empirical formula

$R_2S_2HgI_2R$ . They are really disulphonium compounds and are formulated thus :



where R represents an alkyl radicle.

It may be mentioned here that Hilditch and Smiles obtained the same salt by a different method, although they regarded it as a derivative of the monosulphide. (T., 1907, 91, 1397).

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Dr. B. L. Chaudhury vacated the Chair and Dr. P. C. Ray, occupied it again.

*On the occurrence of some gases in magnesite from Salem.*

By JNANENDRA CHANDRA GHOSH and others.

The presence of gases in rocks and minerals has been extensively investigated by Ramsay, Travers, Tilden, Guitor, etc. Helium has been found in radioactive minerals, hydrogen, carbon monoxide, etc.

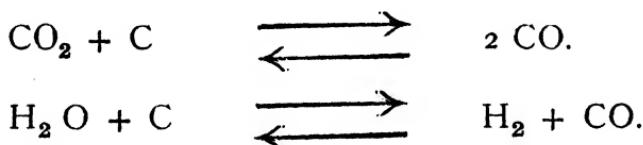
In the course of an estimation of nitrogen by Duma's method, it was noticed that if Salem magnesite be substituted for  $NaHCO_3$  the apparatus could not be completely freed from gases insoluble in KOH, at the initial stages of the experiment. This led to a suspicion, that magnesite on heating gives off besides  $CO_2$ , a gas insoluble in lye.

Further experiments to determine the nature of this residual gas were thus carried out :—A piece of magnesite was freed from all sources of extraneous contamination by striking off the superficial parts with a porcelain pestle, and then ground to powder in a

porcelain mortar. The combustion tube was subjected to a preliminary heating for an hour in a current of  $\text{CO}_2$  to drive off all gases adsorbed on its surface. It was then filled with magnesite and the air inside chased off by a current of  $\text{CO}_2$  obtained from a  $\text{Na HCO}_3$  tube attached to it. The gas generated by heating magnesite was next collected over lye. The residual gas was found to be partly soluble in ammoniacal cuprous chloride solution ; the insoluble part exploded with oxygen, but the reaction products did not give any test of carbon dioxide. The gas therefore is probably a mixture of hydrogen and carbon monoxide.

Again on dissolving magnesite in hydrochloric acid, a gas is obtained which is not soluble in KOH solution. The nature of this gas is also under investigation.

The presence of hydrogen and carbon monoxide may be explained by assuming—Firstly that they remain occluded in the mineral ; Secondly that a chemical reaction takes place between carbon dioxide, moisture, and the carbonaceous matter that may be present in this sedimentary rock thus



Experiments are in progress to determine which of these hypothesis is the correct one.

An analysis of the sample of magnesite by Dains, will prove interesting,—

Silica— $0.29\%$	Iron oxide and	Alumina— $0.3\%$
$\text{MgO}$ — $47.35\%$	$\text{CO}_2$ — $51.44\%$	Combined water— $0.27\%$

PROCEEDINGS  
OF THE  
**INDIAN ASSOCIATION FOR THE CULTIVATION OF SCIENCE.**

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Vol. I.

No. 4.

Wednesday, December 22nd, 1916, at 5 P.M.,  
C. V. Raman, Vice-President, in the Chair.

*On the Ancient Hindu conception of Ether.*

By MANINDRA NATH BANERJEE, F.C.S.

Preliminary note.

*Ether in the Vedas*—

*Yaska* mentions sixteen synonyms of *ether* in the *Vedas*. They are :—

अम्बरम् (ambaram), बियत् (biyat), ब्योम् (byoma)  
बहिः (barhih), धन्व (dhanva), अन्तरिक्षम् (antariksam),  
आकाशम् (ākasam), आपः (apah), पृथिवी (prithivi), भः  
(bhuh), स्वयम्भूः (svayambhuh), अध्वा (adhva), पुष्करम्  
(puskaram), सगरः (sagarah), समुद्रः (samudrah),  
अध्वरम् (adhvaram)\*. The explanation of each of these terms as rendered by some of the oldest vedic commentators has been fully given in the original paper of which this is a mere abstract. But it may be interesting to bring forward the term '*adhvaram*' allied and akin to the Greek '*aether*'.

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\* निघंतु Nighantü—I,3.

The Sanskrit term *adhvaram* means 'upper air.' The Greek term '*aether*' means 'upper air.' From the similarity in meaning and construction we are inclined to think *adhvar* and *aether* to be allied terms. But after its use in the *Vedas* (Rig-veda 8,3,23,3,), its occurrence in any other branch of Sanskrit Literature as a synonym of '*ether*' has not yet been, so far as our investigation is concerned, discovered and for this reason, it seems to us, there is no mention of such a term in the famous lexicon *amarkosa* along with the synonyms of *akasam*.

Again the idea of a fifth material element like *ether* in the comparative ancient literature is, as far as our investigation is concerned, nowhere found. The *Chow*, the famous Chinese ancient literature of about 2,000 years B.C. in its 4th Book on science and allied subjects does not mention anything about *ether* as it describes the characteristic qualities of five elements, viz., earth, water, fire, wood and metal. The Babylonian, the Phoenician and the Egyptian literature also do not give us the idea of a fifth element. While in the earlier Greek Literature we have also the idea of four elements only. So we fail to recognise in the ancient literature, except in the *Vedas* and their allied branches, the conception of a fifth element like *ether*. Plato, in his dialogues—“*Timaeus*,” makes the mention for the first time of the term *ether* and Aristotle, quite originally though, deals with it in his IV Book of Physics by an elaborate argument on the “*Plenum* or *Vacuum*, i.e., space surrounding the universe.” Thus here for the first time we see the idea of a fifth element introduced into European Literature.

One of the vedic commentators\* explains the term '*adhva*' from which the term *advar* is said to be derived, saying that *it is that through which the sun constantly travels, i.e., it is one which allows passage to the sun.* We are apt by our prejudices to credit the belief that in the vedic times the people had no clear knowledge of Astronomy as they considered the sun to revolve round the earth and thus interpret the meaning of '*adhvar*' as rendered by the above commentator to be allowing passage to the moving sun in his usual revolutions round the earth. Such interpretations, however, cannot be accepted in the face of the definite mention in the Vedas—“**स वा एष न कदाचनास्तमेति**” (*Sa ba esa na kadacanastameti*) meaning that '*the sun never sets*'. Dr. Martin Hauq commenting on this passage observes—“ This passage is of considerable interest containing the denial of the existence of sunrise and sunset. The vedic author supposes it (the sun) to remain always in its position in the sky \* \* \* \*. ” The same view may be supported from an observation of Dr. Monier Williams in his 'Hindu Wisdom' where he says—“ We may close the subject of the Brahmanas by paying a tribute of respect to the acuteness of the Hindu mind which seems to have made some shrewd astronomical guesses more than 2000 years before the birth of Copernicus.” Thus from a consideration of all these assertions and various other arguments and evidences the meaning of *adhva* as giving passage to the sun may be interpreted to express as *transmitting the sun's rays* which is clearly supported by the explana-

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\* Vide—*Nirukta. Bibliothica Indica* (Asiatic Society of Bengal).

tions of other synonyms of ether such as, आकाशम् (*ākasam*), पुष्करम् (*puskaram*), ब्योम् (*byoma*), वियत् (*biyat*), etc.

In using the commentaries on the Vedas we have not only followed 'SAYANACARYA,' the great vedic commentator who is, unfortunately, not much thought of by such critics as Vincent Smith, but we have also tried to closely and freely adopt the views of such earlier vedic commentators as *Yaska* himself, *Skandasvami*, *Bhavasvami*, *Rahadeva*, *Srinivasa*, *Madhava-deva* (not *Sayana-Madhava* of later times), *Ubatabhatta*, *Bhaskaramisra*, *Bharatasvami*, as well as those of the Nirukta commentaries of *Skandasvami* and Nighantu commentaries of *Ksiravami* and *Anantacarya* not excepting the vedic commentary of the great author of *Vedadipa*, viz., *Mahidhara*.

Thus following, one could see through the *Vedas* a very ancient conception of "ETHER", as an all-pervading, all permeable, highly rarified substance, the means of transmission of light rays, a fifth state of material existence to which everything is reducible, and which was considered to be the primordial matter having motion and energy (sometimes identified with electricity itself) though it can never combine with any other body, and such a view of 'the ether' permeates through the whole length of Sanskrit Literature as is evidenced by the well-known expression in our BHAGAVAT GITA—

“यथा सर्वगतं सौकृत्मादाकाशं नोपलिष्यते  
सर्वव्यावस्थितो इहे तथात्मा नोपलिष्यते” (१३-३३)

[‘‘Yatha sarvagatam sauksmyādākasam nopalipyate Sarvatrābasthito dehe tathātmā nopalipyate”—13. 33.], which has been rendered by a renowned English scholar \* thus—“As the *omnipresent* ether is not affected by reason of its *subtlety*, so seated everywhere in the body the self is not affected.”

#### ETHER IN THE VEDANGAS AND THE DARSANAS.

After the vedic period we have tried to give an account of the conception of ETHER in the Vedangas as *Manusmṛiti* and other *Granthas*. Then we have attempted to project the views on ETHER of the various schools of Indian Philosophy—viz., I—The Vedānta system of Vyasa, II—The Yoga system of Pātanjala, III—The Sankhya system of Kapila, IV—The Mimāmsā system of Jaimini, V—The Nyaya system of Gotama, and VI—The Nyaya-Vaisesika system of Kanāda. The whole of this literature from the days of Manu up to later times endorses fully the earliest vedic conception of ETHER and not a line of this could be construed to mean by any one to be a mere metaphysical working hypothesis of more or less of the character of fantastical dreams of the ancient Hindu philosophers.

#### ETHER IN THE COMPARATIVE LITERATURE OF THE ANCIENT PEOPLE OTHER THAN INDIANS.

Next we proceed to describe the Chinese, the Egyptian, the Babylonian and the Phoenician conception of the elements and try to shew that the idea of a fifth element like that of *ether*, is altogether wanting in them. The same is the case with the Greek schools

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\* Mrs. Annie Besant.

of Thales, Anaximander, Heraclitus, etc., until in Plato's dialogues (in Timaeus) we find the mention of 'Ether' or 'upper air', a full exposition of which is dealt with by Aristotle in his Physical auscultation, Book IV. *According to Aristotle every material body must have an etherial system before or it might be reducible to ether.*

#### VIEWS OF LATER PHILOSOPHERS.

After Aristotle natural philosophers theoretically supposed space to be filled with some rarified residues of vapours or gases. And this view even corresponds with Kant's, Laplace's and other theories which aim at explaining the unity and plan in the creation of the heavenly bodies. The same theory also explains the uniformity of chemical composition of the entire universe which has been practically supported by the spectroscopic demonstrations of the later periods and which offers 'a means of interchange between heavenly bodies through the agency of *Ether*'. Later on, the idea of subjecting the conception of ether as a rarified gas to experimental investigation and measurement troubled many scientists. But, however correct this idea might be, as it alone could direct the mind to the right direction and lead to reliable results, it has to be given up owing to certain practical impossibilities that came in the methods of measuring pressures with any degree of accuracy under tenths of a millimetre of mercury.

#### VIEWS OF MODERN SCIENTISTS.

In the days of Galileo, Newton and Lavoisier, the natural science seemed to be somewhat sceptical about

the conception of ether as a rarified gas. But later on, Lord Kelvin from various considerations attributed ether some weight and came to the conclusion that a cubic metre of ether must weigh less than 0'000 000 000 000 000 1 gram while a cubic metre of hydrogen weighs 90 grams under the atmospheric pressure. Proceeding on this idea and on the facts of the discovery of the natural classification of chemical elements and of the inert group of gases, as well as of radium and radio-active properties of some elements, Mendeleeff was led to formulate a purely theoretical conception of ether, thus—*That it is an elementary gas like helium or argon, incapable of chemical combination, which he termed x and assigned to it a position in the periodic table high above in the Zero group of elements. That the particles and atoms of this lightest element x, capable of moving freely everywhere throughout the universe, have an atomic weight nearly one millionth that of hydrogen and travel with a velocity of about 2,250 kilometres per second.*

Sir James Dewar in his Presidential address of the British Association at its Belfast meeting in 1902, lent a thought of his to the idea that the highest regions of the atmosphere which are the seat of the Aurora Borealis must be considered to be the province of hydrogen and of the argon and its analogues. This, some of the leaders of contemporary sciences supposed to be only a few steps from the yet more distant regions of space and from the necessity of recognising the existence of a still lighter gas capable of permeating and filling space and thus giving a tangible reality to the conception of the ether.

ANCIENT HINDU CONCEPTION OF ETHER COMPARED TO  
THAT OF MODERN SCIENCE.

But, however, valuable and important the various theoretical speculations of a large number of thoughtful scientists might be regarding the conception of ether, it must be said that modern science has not been able to proceed a step further beyond the views promulgated in the earliest statement concerning ether in the Vedic and allied branches of ancient Hindu Literature.

P. Larousse, as we learn in his 'Dictionnaire complet' defines ether as an imponderable, elastic fluid filling space and forming the source of light, heat, electricity, etc.' But, "the modern thoughtful man of science," as Mendeleeff observes, "is obliged to admit in the ether, the properties of a substance (fluid), while at the same time, in order to explain in some way the transmission of energy through space by its motion the ether is assumed to be an all-pervading 'medium,'" —a conception which vie equally with that mentioned in the earliest Sanskrit Literature by the Hindu Risis of yore ; while the latest attempt of the modern scientists, such as, Mendeleeff, Dewar, J. J. Thomson, Lodge, and others to identify *ether* with the *primordial matter* had its clear support from the views long expressed by the Hindu savants which fill nearly the whole range of their literature, as even in 'Surya Siddhānta' we find—

“मनसः खं ततो वायूर्ग्निरापोधराक्रमात्  
गुणैक दृष्ट्वा पच्चैव महाभूतानि जज्ञारे” ॥ १२, २३ ॥ \*

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\* Cf. Manu I, 19 and 20; also I, 75 to 78,

[“*Manasah kham tato bayuragnirapodharākramāt Guṇaika bridhya panceiba mahabhūtani jagñire*”—12,23], meaning—‘from mind by degrees came forth *the ether* therefrom *the air, the fire, the water* and *the earth*. The five great elements thus are formed by the gradual increase of one additional property in each.’

#### CONCLUSION.

A forgotten chapter in the history of physical science consists in the total ignoring of the important facts concerning the ancient Hindu conception of matter. Such ignoring of historical facts is due to the imperfect notion of the ancient Hindu conception of elements, the actual meaning of which the modern scientific world could not either thoroughly grasp or hold out being, as it believes, incongruous to present views on the subject. But whatever incongruity may be noticed in the conception of elements of some of the civilised races of the ancient world, we may, without any fear of contradiction, say, after a careful study and comparison of the various ancient doctrines relating to the subject, that the Hindu conception stands apart as significantly sublime in its essence as accurate in its scientific acumen as could be expected of so high and perfectly scientific a race (as even some foreign savants consider the ancient Hindus to have been), who contributed so much to the illuminating civilisation of the ancient times on earth. But quite ignorant of this led a Kopp or Wheywell or a Cajori or Ball or even a master-mind as Ernst von Meyer to belittle or ignore the ancient Hindu conception of elements, until lately at the instance of that noble minded citizen of France—the world renowned

Berthelot—attention of the European savants was drawn, to some extent, to the brilliant essay on Hindu Chemistry by our most revered countryman, Dr. P. C. Ray, which led Sir Henry Roscoe to give a complimentary note on it in his first volume of Chemistry. Yet, this is but a pioneer work only. The scientific world of modern days is still in the dark about the ancient ideas of matter, it, therefore, behoves us to project them by degrees after a thorough and searching enquiry into the various branches of our Sanskrit Literature—the well of scientific facts undefiled, which now remains unexplored. The faithful expounding of our ancient literature by our own countrymen, thoroughly conversant with modern sciences, could alone remove doubts and controversies on many points of Hindu-Oriental research which, owing to ignorance of the actual Hindu traditions and a true knowledge of Hindu religion, Hindu heredity of life, etc., has hitherto been a cypher to most of the foreign scholars.

### *Action of Strychnine on the Dying Heart*

By Prof. N. C. BHATTACHARYYA, M.A., P. DASS GUPTA, B.Sc., and N. N. MITRA, B.Sc. of the Presidency College, Calcutta.

A white rabbit was anaesthetised with ether; the chest was then opened and the heart exposed. It was not beating then. After opening the pericardium the volume of the heart increased considerably and within half a minnte the heart began to beat, at first slowly then normally; after ten minutes the heart began to sink; the beats became weaker and weaker; the ven-

tricles could not follow the auricular contractions. The number of beats at this period was as follows :—

No. of Ventricular beats per minute	No. of Auricular beats per minute
26	139

Now the effect of strychnine on the heart was tried ; and the great sensitiveness of the preparation was first noticed. The sinking heart seems to be more susceptible to drugs than any other preparation. The animal was lying in a supine position ; the chest cavity formed a sort of basin in which the heart was lying. The basin could contain about an ounce of normal saline and the lower half of the heart remained submerged in the solution. The effect of strychnine was now tried. A 0.5 per cent. solution of the drug was ready. A drop of this was mixed with an ounce of normal saline. The chest cavity was then emptied of any previous fluid and the strychnine solution was then poured on the heart. After one minute the beats were counted. In the succeeding observations the number of drops of strychnine per ounce of normal saline was gradually increased. The most interesting thing noticed was that the strychnine behaved differently with the auricles and the ventricles. It increased the ventricular beats but decreased the auricular contractions, both in number and force. It tends in the case of sinking heart to remove the arrhythmic condition of the heart and bring it to a condition of rhythmicity. As will be seen from the table below, it was found that with a sufficient large dose of strychnine the heart began to beat rhythmically, the ventricles following all the auricular beats.

When the dose of strychnine was increased beyond a certain limit the heart stopped. But from this condition even, the heart was revived several times by washing it with normal saline. And when the heart recovered from the effect of strychnine the same arhythmic condition was again produced. The more the strychnine was washed away the greater was the discrepancy between the auricular and ventricular beats. When strychnine was again supplied to the heart, rhythmic condition was again produced ; the ventricular contractions increased and the auricular contractions decreased in number.

Now the question is, whether the strychnine acts by stimulating the nerve centres in the heart or by stimulating differently the auricular and ventricular muscle fibres. If the last view is true it would suggest that there is some difference in these fibres either in structure or in chemical composition ; but—this does not seem to be warranted by our present knowledge of the subject. But there seems to be a serious draw-back about the nervous-control-theory. After opening the chest of the animal no artificial respiration was started. So the animal was really asphyxiated during the period of experiment. The peculiar strychnine effect could be obtained even after two hours. It is doubtful if the nerve cells would remain alive, so long after respiration was stopped. In the present case the rabbit's heart lived for over two and half hours. Probably the peculiar climatic condition of the tropic helped the heart to last longer. The atmosphere here at Calcutta during rainy season is saturated with water vapour ; evaporation of water is

very slow. The temperature of the room where the experiment was performed was 30.5°C.

### TABLE.

*Observations on Rabbit's heart "in situ"; chest opened.*

Ventricular beats per minute.	Auricular beats per minute.	
26	139	(i) The heart was washed with normal saline.
21	43	(ii) A drop of strychnine (0.5% sol.) mixed with an ounce of normal saline was allowed to fall on the heart. Each observation is taken after an interval of one minute.
28	45	
17	103	(iii) The heart was again washed with normal saline.
24	59	
21	53	
21	44	
28	106	(iv) Strychnine was added.
21	57	
28	46	
24	45	
21	45	(v) Stronger solution of strychnine added.
24	38	
21	43	
19	38	
21	21	

12	12	(vi) More strychnine added to
2	2	the basin.
0	0	
10	10	(vii) The heart was repeatedly
30	30	washed with normal saline.
24	44	
28	76	
28	88	
26	92	
30	84	(viii) Strychnine was again
28	46	added.
34	34	

### SUMMARY.

1. In Calcutta during the hot part of the rainy season an exposed rabbit's heart lasts for over two hours.
2. Such a heart preparation is gradually dying. It forms an exceedingly sensitive preparation for studying the action of drugs ; changes in the heart can be easily followed by the eye.
3. If strychnine be applied to a sinking heart which has lost its rhythmicity, it improves the ventricular beats both in number and force and restrains the auricular contractility by decreasing the number of auricular contractions.

In conclusion, our best thanks are due to Professor S. C. Mahalanobis, for his kind guidance during the work.

Mr. Narendra Mohun Bose of the Physiological Laboratory, Presidency College, observed that Prof. Bhattacharya wanted to establish in his paper the two following points from his observation on the action of strychnine in normal saline upon the exposed heart of a rabbit. These are :—

- (i) The mammalian heart can beat for a long time after the chest wall is opened, provided it is washed with normal saline, or better with a weak solution of strychnine in normal saline.
- (ii) The action of strychnine on the auricles and ventricles is not the same. It promotes the ventricular contraction but decreases the auricular contraction.

The first point is really quite interesting, although it has been noted in Leonard Hill's "Further Advances in Physiology" p. 58, that the mammalian hearts can be revived many days after death. I do not remember to have seen in any book that such hearts can be revived, when the chest wall is opened, without perfusion of normal saline but simply by washing with Ringer's fluid or normal saline.

As regards the second point, I am rather chary in accepting it. The observations upon which this is based are, I suppose, capable of a better explanation. Prof. Bhattacharya noticed after removing the chest wall of a deeply anaesthetised rabbit—

- (a) that the heart was lying still ;
- (b) that after it was washed several times with normal saline solution it began to beat but there was no rhythm between the auricular and the ventricular beats—the

former being much more frequent than the latter;

- (c) when it was flushed with weak strychnine solution in normal saline, the number of auricular beats became very much less and that of the ventricular beats greater than before but the rhythmicity was not established;
- (d) when strong strychnine solution in normal saline was used rhythmicity was established, but the frequency of the auricular beats became much less than before.

All these phenomena can be explained if we assume that the strychnine is a stimulant of muscular activity in small doses, but acts as a protoplasmic poison in higher doses.

- (a) The quiescent state of the heart that was noticed when the chest wall was removed is certainly due to the overdose of ether or chloroform which was used for anaesthetising the animal (vide Further Advances in Physiology—pp. 4-5).
- (b) When the heart was washed with normal saline the osmotic pressure of the anaesthetic in the cardiac cells diminished and the heart recommenced its beating. The arrhythmicity of beats that was noticed between the auricles and the ventricles must certainly be due to some block either in the A-V Bundle of His or in the A-V node, or in the ventricular musculature for otherwise the ventricles would have

taken up the rhythm of the auricles as they do in the normal heart.

(c) When the heart was washed with solution of strychnine, this block was partially removed as the auricular contractions became more forcible owing to the stimulant action of the drug. As a result of this the number of the ventricular beats increased, but the cause of the simultaneous diminution of the auricular beats is to be found in the poisonous action of the drug in consequence of which the cardiac muscle cells were gradually dying away.

(d) With the stronger solution of strychnine the contraction became still more powerful, so that the block was removed and the rhythmicity was established. But at the same time the poisonous effect of strychnine became more manifest and consequently the auricular beats became much slower.

In conclusion Mr. Bose said :—The theory suggested by Prof. Bhattacharya as an explanation of his observations may hold good, but the explanation suggested above is more probable than the one put forward by Prof. Bhattacharya.

The Chairman observed that the study of the curves recorded by the rabbit's heart under the condition described by the Professor might be of great interest and that electro-cardiograms might also be taken and studied.

*On the Crystalline Limestone from Daltonganj.*

BY HEM CHANDRA DAS GUPTA, M.A., F.G.S.

*Introduction.*

In the maps of the Daltonganj coalfield published by Hughes to accompany his memoir on that area <sup>(1)</sup>, mention has been made of the existence of a band of crystalline limestone lying just along the boundary between the Talchirs and the Archaeans; but as Hughes' main purpose was to describe the coal measures nothing has been said about the gneisses and the associated crystalline limestone. A second report on the Daltangonj coalfield appeared later on <sup>(2)</sup> in which Mr. LaTouche recorded the results he obtained from boring operations in the area. There is a map accompanying this paper and the band of the crystalline limestone is marked on it also. There is no description of the limestone but a study of his map shows that the crystalline limestone lies (i) along the faulted boundary between the Talchirs and the Archaeans and (ii) within a small zone which has been considerably deformed, as indicated by a difference of dip of  $20^{\circ}$  within a distance of quarter of a mile. About a year ago I had an opportunity of visiting this band of crystalline limestone and the results of my study are recorded in this note.

*Associated rocks: Granite-gneiss. Pyroxene-granulite.*

The band of crystalline limestone is rather narrow and extends over a mile. At some places the limestone is succeeded by a granite gneiss while at other

(1) Mem. Geol. Surv. Ind. Vol. VIII pp. 325-346.

(2) Rec. Geol. Surv. Ind. Vol. XXIV. pp. 141-153.

places it is associated with a garnetiferous rock, the latter rock, in its own turn, being followed by the granite-gneiss. The granite-gneiss is of the type usually met with in the Bengal Archaean area and there is nothing peculiar about it. The felspar includes a potash-bearing one, microcline. The garnetiferous rock just mentioned may be described as a pyroxene-granulite. It is highly basic with a specific gravity of about 3·3. In one place the pyroxene-granulite was observed to be associated with crystalline limestone while at another place no such association could be seen and specimens, collected from these two localities, appear very different especially when examined under the microscope. In both rocks the chief constituents are garnet, green non-pleochroic pyroxene, a very small amount of secondary hornblende, basic plagioclase felspar and a very highly refracting substance doubtfully identified as zircon. The difference in the two rocks is found, however, chiefly in the different types of pyroxene. In the granulite not associated with the crystalline limestone the pyroxene patches are fairly big, while in the granulite associated with the limestone the pyroxene crystals appear to be drawn out, showing that the latter have undergone much crushing. The garnet of the latter rock also appears to be somewhat broken, but the evidence is not conclusive.

#### *Crystalline limestone : Ophicalcite.*

The limestone is thoroughly crystalline, granular and varies in colour, being grayish but always with a greenish tinge. Specimens of the rock were collected from three different localities, namely from the two

extremities of the exposure as also from the place where it lies in association with the pyroxene-granulite above referred to. All these rocks stain beautifully red with Lemberg's solution so that the rock is mainly composed of calcite. Besides calcite the other important mineral is serpentine, occurring generally in round and ovoid patches with some small amounts of muscovite here and there. The rock can, I think, unhesitatingly be described as an ophicalcite.

#### *Ophicalcite : Previous Indian records.*

Ophicalcite or serpentinous limestone has already been recorded from many Indian localities, e.g., from Western India<sup>(3)</sup> from Hazaribagh<sup>(4)</sup> and Chhindwara<sup>(5)</sup>. The occurrences in the last area have been very thoroughly described by Dr. Fermor and here besides the three different classes of crystalline limestone, calciphyre has also been obtained.

#### *Ophicalcite : Origin of Serpentine.*

Serpentine is one of the commonest secondary products of magnesium-bearing silicates, there being quite a number of minerals from which it may be derived and they include olivine, pyroxene, amphibole and garnet. There is no restriction whatever as to the type of the magnesium-silicate from which the serpentine of ophicalcite may be obtained. Zirkel<sup>(6)</sup> has described an ophicalcite in which the serpentine has been found to be derived from olivine. An

(3) Mem. Geol. Surv. Ind. Vol. VI. p. 321.

(4) Mem. Geol. Surv. Ind. Vol. XXIV. p. 41.

(5) Rec. Geol. Surv. Ind. Vol. XXXIII pp. 162-220,

(6) Neu. Jahrb XX (pp. 828-832, 1870).

ophicalcite has been described by Prof. Kemp<sup>(7)</sup> the serpentine of which has, nearly in all cases, been derived from colourless pyroxene, but in several instances the unchanged core of the serpentine has been found to be an isotropic mineral of a high refractive index. This substance, according to Prof. Kemp, may very probably be a garnet. Merrill<sup>(8)</sup> has described an ophicalcite in which the serpentine is an alteration or a metasomatic product after a mineral of the pyroxene group. Two types of ophicalcite have been recorded from the Anglesey area and the serpentine of one of them is supposed to have been infused from without<sup>(9)</sup>.

#### *Daltonganj ophicalcite: Evidence of origin.*

Any theory about the origin of ophicalcite must satisfactorily account for the origin of calcite and of serpentine, the chief constituents of the rock. In order to decide this question I had a number of slides prepared and I was fortunate enough to come across a few which I hope throw some light on this genetic question. One of the slides thus examined shows a fairly big white pyroxene undergoing alteration into calcite and serpentine. The same feature is also observed in another slide but not so markedly. There is another section which, besides calcite, serpentine and a few patches of muscovite, contains some non-pleochroic bright patches of high refractive index and which appear to me to be nothing but garnet.

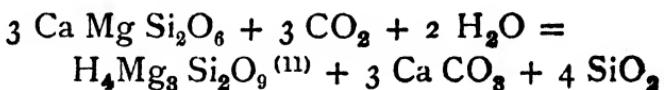
(7) Bull. Geol. Soc. Amer. Vol. VI pp. 221-262, 1895.

(8) Amer. Journ. Sci. 3rd Ser. Vol. XXXVII pp. 189-191, 1889.

(9) Rep. Brit. Assoc. Adv. Sci. 1888 p. 409.

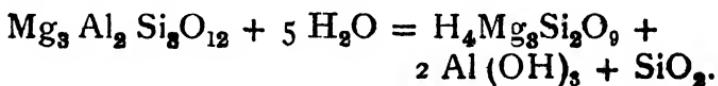
### *Alteration of Pyroxene.*

It is well known that pyroxene alters into a number of minerals and among these alteration processes may be mentioned the simultaneous production of calcite and serpentine. An alteration like this has been described by Dr. Fermor from the Chhindwara area<sup>(10)</sup> the equation, representing the change according to Van Hise, being :—



### *Alteration of garnet.*

There is a large number of minerals into which garnet may be changed and a list of these alteration products is to be found in the monograph of Van Hise on metamorphism. One of the commoner products is serpentine, the change being supposed to take place according to the following equation :—



### *Optical anomaly of garnet.*

Mention has been made in a previous paragraph of the existence of garnet in a slide. This slide contains only a few patches of unaltered garnet and an examination of these shows that some patches are strongly doubly refracting though there is at least one patch which is practically isotropic. Optical

(10) Op. Cit. p. 171.

(11) D. Fogy has tried to prove that the formula of serpentine should be  $\text{Si}_4\text{O}_{12}(\text{MgOH})_6 \text{H}_2$ . (Sitzb. d. Math-Nat. Kl. K. Akad. Wiss Bd. CXV. Abt. I. pp. 1081-1085, 1906).

anomaly of garnet has been known for a very long time and there has been a good deal of investigation regarding the cause of the anomaly. In this connection mention may be made of an augite-garnet rock described by Von Federow<sup>(12)</sup>. This rock is of eruptive origin with a tendency to metamorphism and, as a result of this metamorphism, garnet has been changed to epidote and augite to chlorite and secondary hornblende with the separation of calcite and quartz. Thin sections of this rock examined under microscope show that there are two different types of garnet one of which is brown and the other colourless. The brown substance is optically normal but the colourless one shows anomalous optical properties as a rule. The chemical composition of these two garnets is very nearly the same but there is a difference in their specific gravity. As a result of his investigations into the cause of this anomaly in the behaviour of garnet Von Federow supposes the phenomenon to be certainly due to some changes in the molecular volume of the mineral——‘und zwar die relative Aenderung des Molekularvolumens’. According to him ‘die Ursache kann allein eine solche sein, welche von den mechanischen, bei der Deformation der Form entstehenden Kräften abhängig ist.’

*Optical anomaly of garnet in the ophicalcite of Daltonganj.*

From the above considerations it is quite clear that the optical anomaly of garnet may be due to a variety of causes and in the same rock there can occur garnet

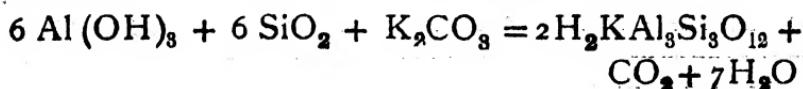
both isotropic and anisotropic. The zone where the Daltonganj ophicalcite occurs is one which has undergone some disturbance, though the disturbance might have been quite local in character. Isotropic substances when under considerable stress in any one direction become anisotropic and accordingly there is no wonder if at least a few of the garnets which are in the process of alteration show some anomalous character under the crossed nicols.

*Ophicalcite: Suggested origin.*

It appears to me from the study I have made of this crystalline limestone that we may suppose it to be derived from the alteration of a pyroxene-garnet rock. Under this hypothesis the calcite is derived from the alteration of pyroxene and serpentine mainly from garnet, but also to a small extent from pyroxene.

*Presence of muscovite.*

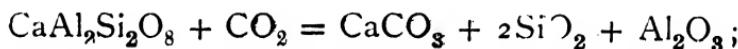
From the equations given above regarding the alterations of augite and garnet it will appear that secondary silica and gibbsite are also produced. These substances have not been observed in the sections examined but they, according to Van Hise, may be dissolved and transported elsewhere so their absence is no proof that these substances were not actually formed during the alteration. Mention has been made of the presence of muscovite in some of the slides and it is just possible that at least a part of this secondary gibbsite and silica has been changed into muscovite according to the following equation :—



The potassium-carbonate required for this change might have been derived from the potash-felspar observed in the granite-gneiss and mentioned before.

*Alteration from pyroxene-granulite.*

I think that there is no reasonable ground for doubting that the ophicalcite is a secondary rock and that it has been derived from a previously existing rock consisting of pyroxene and garnet. The occurrence of pyroxene-granulite in immediate association with the crystalline limestone has been noted above and it has been observed that the pyroxene affords evidence of being much broken. Besides pyroxene and garnet the rock contains basic plagioclase felspar and this is also liable to be changed to calcite according to the following equation :—



the alumina, as suggested by Dr. Fermor<sup>(13)</sup>, may be subsequently supposed to be removed in solution as an alkaline aluminate. From these considerations and further from the fact that no other pyroxene-garnet bearing rock lies in the neighbourhood, the derivation of this ophicalcite from the pyroxene-granulite may be suggested as a plausible hypothesis.

*Cementation.*

There is however one difficulty which presents itself regarding this hypothesis. The pyroxene of this pyroxene-granulite is green coloured and occurs in small grains while the pyroxene referred to in the first slide examined is rather large and white, though in this slide pyroxenes of smaller size are also present.

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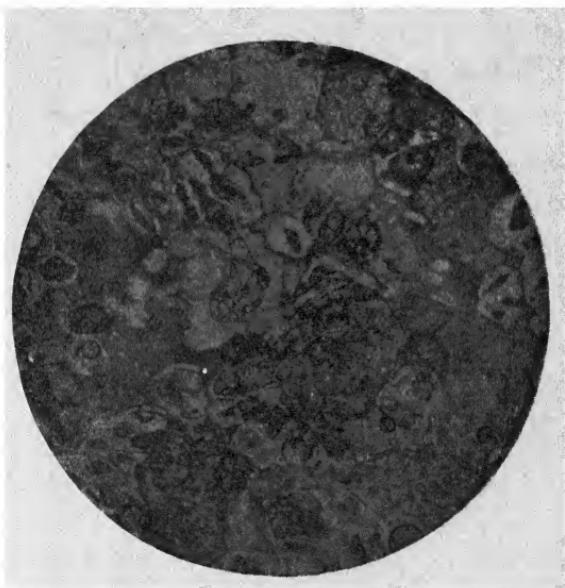
(13) Op. Cit. p. 194.

If we suppose, however, that the individual small grains of pyroxene of pyroxene-granulite were cemented prior to re-crystallization so that the enlargement is due to cementation this difficulty may be overcome while decolouration has very often been noted as a result of metamorphism.

*Summary.*

The purpose of this short note is to put on record that (1) the crystalline limestone of Daltonganj is in the main a serpentinous limestone or ophicalcite; (2) this ophicalcite is derived from a pre-existing pyroxene-garnet bearing rock and (3) this pyroxene garnet bearing rock may be the pyroxene granulite associated with the ophicalcite.

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X 22

Ophicalcite showing the ovoid patches of *garnet* changing to *Serpentine*.













